Birmingham Section.

Meeting held at Birmingham University, on Thursday, December 10th, 1914.

MR. H. T. PINNOCK IN THE CHAIR.

POLYMERISED DRYING OILS.

BY R. S. MORRELL, M.A., PH.D.

When linseed oil is heated it gradually thickens and grades of "litho oils" are produced depending on the temperature and the duration of the heating. According to Lewkowitsch (Oils, Fats, and Waxes, 4th ed., Vol. 3, 95), the thickening is a polymerisation process. There is no appreciable oxidation, but the iodine value is lowered and the oil no longer gives a crystalline hexabromide. The " litho oils " (burnt varnishes) dry fairly quickly at the ordinary temperature, but in the thick lithos the drying power has much deteriorated. The glyceryl radicle of the oil is unaltered in the process. Lewkowitsch states that the chemical changes are not yet fully understood and they may be conveniently summarised under the term polymerisation. Safflower, sterculia, poppyseed, and castor oils also thicken when heated, and in the case of Chinese wood oil (tung oil) the thickening is very rapid and is difficult to control. The final stage is the production of a gelatinous mass, solid in the case of tung oil, which is insoluble in ordinary solvents, but easily saponified by alcoholic potash. The acids obtained from the above oils possess in like manner the property of thickening when heated.

Litho oils have been studied by a number of investigators, among whom may be mentioned Lewkowitsch, Normann (Chem. Zeit., 1907, 188 ; see this J., 1907, 262), Fahrion (Farbenzeit, 17, 2530 ; see this J., 1913, 95); Schafringer, Rassow, Wolff (Farbenzeit, 1913, 1171; see this J., 1913, 496), and Fokin (J. Russ. Phys.-Chem. Soc., 1913, 45, 283; see this J., 1913, 496).

Fahrion considers that the polymerisation of tung oil proceeds on the same lines as in the case of linseed oil and that there are indications of mixed glycerides in the oil taking part in the polymerisation.

Schafringer (Dissert., 1913, Freiburg) summarises an investigation on the thickening of castor, linseed, and tung oils. He states that castor oil polymerises to a viscid mass on partial distillation, whereby part of the glyceryl radicle is expelled, but the iodine value is unaltered, showing that polymerisation has not occurred at the position of the double linkages. Linseed oil thickens by union at the double linkages of the molecules and not through oxidation ; most probably the linolenic glyceride is the first to be changed. Wood oil thickens similarly to linseed oil and the process may proceed in two stages, of which the first gives at one and the same temperature the same intermediate product, but at different temperatures different intermediate substances are formed. The polymerisation is in no case reversible.

Rassow (Z. angew. Chem., 1913, 26, 316) has shown, in the case of castor oil or ricinoleic acid, that di- and poly-ricinoleic acids are formed whose iodine values are the same as that of the original

acid, but the acid values have been reduced to one half (or less) that of the parent acid. He assigned to di-ricinoleic acid the formula,

$$HO.C_{17}H_{32}COO.C_{17}H_{32}COOH.$$

Instances of the polymerisation of substances containing unsaturated groupings are so numerous that mention need be made of only one case which seems relevant to the study of litho oils.

Kronstein (Ber., 1902, 35, 4153) has investigated the polymerisation of styrol ($C_6H_5CH : CH_2$), which proceeds in two stages. The first stage is a gradual thickening, followed by gelatinisation, which constitutes the second stage. The product of the second stage is insoluble in benzol. The gelatinisation is accompanied by evolution of heat and occurs when half the styrol has passed into the intermediate stage, showing that the gelatinisation must have been produced by union of monomolecular styrol with the intermediate polymeride. Depolymerisation takes place on further heating, and when 50 % of the styrol has been distilled off the residue consists of the intermediate substance. Further heating decomposes the styrol molecule.

It has been noticed by investigators that the final product of the thickening of linseed oil is insoluble in light petroleum, and in this communication the results of the study of an intermediate product, soluble in light petroleum but insoluble in acetone, will be described. Similar intermediate products have been obtained from poppyseed and tung oils.

Experimental.

Linseed oil from various sources was thickened in bulk or in smaller quantities in the laboratory, and to avoid oxidation the operation was performed as far as possible in an atmosphere of carbon dioxide or hydrogen. Hydrogen under ordinary conditions or under pressure without a catalyst is stated to have no action on unsaturated fatty acids (Thorpe's Dictionary, Oils, Fats, and Waxes, 2nd Ed., Vol. 3, 57); nevertheless it was found that under the conditions of the experiments a very slight addition occurred and subsequently carbon dioxide was used instead. The oil was heated for 28—60 hours at 260° C and the thickened oil was completely soluble in light petroleum. In the case of tung oil the temperature and time of heating were 240° C. and 20 minutes, respectively, and the heating was stopped as soon as any of the substance insoluble in light petroleum was formed, in other words as soon as gelatinisation commenced.

A summary of the constants of the oils showed that a considerable change in the chemical and physical properties had occurred.

The fall in the iodine value is essentially a function of the temperature, because linseed oil which has been kept at 260° C. for 28¼ hours, can be heated for a further period of 20 hours at the same temperature without any change, but on raising the temperature to 293° C. and continuing the heating for further 2¼ hours, the iodine value fell to 89—97 and a substance was formed which was insoluble in light petroleum and in carbon tetrachloride. The glyceryl values are not very satisfactory, but considerable difficulty was experienced in getting good results by the acetin method, and the differences are attributed to unavoidable experimental error.

It is evident that one phase of a change in the linseed oil is complete between 260° and 280° C., and that above that temperature another makes its appearance.

	Linseed oil.				Tung oil.	
	Raw.	Thickened in bulk 260°—280° C.	Thickened in hydrogen at 260°—280° C.	Thickened in CO₂ at 260°—280° C.	Raw.	Thickened.
Specific gravity (15° C.)	0·933	0·9527 : 0·969	0·9654	0·969	0·9405	0·956
n_D	1·4831 (19° C.)	—	—	1·4915 (19° C.)	1·5172 (14° C.)	1·5134 (15° C.)
r_D	0·3053 (15° C.)	—	—	0·2998 (15° C.)	0·3140 (14° C.)	0·3117 (15° C.)
Molecular weight (in benzene)	805	—	—	1686—1704	797	1431
Acidity	0·4	5·15	2·4	1·7	3·3	2·3
Saponification value..............	197—203	188—193	195—196	200—203	192—4	190—201
Iodine value	185	103—106	93—128	118—134	165—168	143—171
Glyceryl %	9·62	—	—	10·4	10·47	8·3
Crystalline hexabromide	33·5%	none	none	none	none	none

It was found that the oil, thickened between 260° C. and 280° C., contained two modifications, one insoluble in acetone and the other soluble, but both soluble in light petroleum. These modifications were separated by extracting the thickened oil with hot acetone until no more was dissolved. Five extractions were necessary and about ten times the volume of hot acetone was used. Table 2 gives a comparison of the properties of the modifications. Tung oil shows a similar behaviour to that of linseed oil in furnishing a modification insoluble in acetone. It will be shown later that olive oil does not give an insoluble form, and in the case of poppyseed oil the insoluble modification is not produced below 290° C.

under the investigation of poppyseed oil. The figures given are the extremes, in the case of the iodine values, and the mean in other cases of a large number of determinations, the work of several years. It is noticeable that the 50% transformation resembles the behaviour of styrol.

The investigation of the properties of the two modifications of linseed oil showed that important chemical changes had occurred. The oils (insoluble and soluble in acetone) were transformed into lead or barium salts. The lead salt from the oil, *insoluble in acetone*, was insoluble in ether and the barium salt was only slightly soluble in benzol alcohol (about 17·45 % was soluble) but was insoluble in ether. The lead salt from the

TABLE 2.

	Linseed oil.	Thickened linseed oil.		Tung oil.	Thickened tung oil.	
		Insoluble	Soluble		Insoluble.	Soluble
		in acetone.			in acetone.	
Solubility in acetone	100%	42—60%	41—52%	100%	47·5% (240° C.) 27·8% (210° C.)	46·6% (240° C.) 72% (210° C.)
Sp. gravity (15° C.)	0·933	0·9763 0·980	0·9527 0·9593	0·9405	— —	0·9542 0·9408
n_D	1·4831	1·4964	1·4846	1·5174 (12·5° C.)	—	1·5114 (11·5° C.)
r_D	0·3053	0·2892	0·3035	0·3204 (12·5° C.)	—	0·3143 (11·5° C.)
Molecular weight (in benzol)	805	1788—2517	904—975	797	—	876·2
Acidity	0·4	0·2	7·5—8	3·3	0·567	2·47
Saponification value........	197	190—204	193	192	198·5	192·6
Iodine value	185	97—121	92—143	168	76·5—151	93—140—157

Consideration of the figures in the table allows some important conclusions to be drawn. At 260° C. approximately equal quantities of the two components are present in linseed oil. When tung oil is heated to 240° C. for 20 minutes until gelatinisation commences, or when a substance insoluble in light petroleum appears, approximately equal quantities of the components are present ; above that temperature the oil is no longer completely soluble in light petroleum. The modification insoluble in acetone has a much higher specific gravity. The acidity has undergone no great change, and it is only natural that the soluble oil should have the higher acid value. The iodine values are in all cases lower than those of the raw oils ; they vary with the time of contact with Wijs' solution. Although the iodine values of linseed or tung oil are practically unchanged when the oil is left in contact with the iodine solution for hours or even days, the iodine values of the components may vary by 30—40 units under the same conditions. This variation can be explained by the slow disruption of the polymerised molecules. Consideration of the molecular weight values shows that the first stage is the production of a double molecule, but the part of the oil soluble in acetone has not varied appreciably. The slightly higher value will be referred to later

oil, *soluble in acetone*, was completely soluble in ether (allowing for the presence of the usual quantity of insoluble lead salts of saturated fatty acids present in linseed oil). The barium salt was dissolved by benzol-alcohol and on cooling 15·5 % separated out, consisting of a mixture of an oleic acid with stearic and palmitic acids. The barium salt, soluble in benzol-alcohol, was found to be quite insoluble in ether. Precautions to exclude air and prevent oxidation were taken in all cases.

Barium and lead linolenates and linolates are soluble in ether and in light petroleum. Lead oleate is soluble in ether and barium oleate is very sparingly soluble in benzol-alcohol (Farnsteiner, Z. Unters. Nahr. u. Genussm., 1901, 63) but is insoluble in ether. From the behaviour of the barium and lead salts it was evident that in addition to polymerisation, some linkage movements had occurred either in a displacement relative to the carboxyl group or in a ring formation of the single molecule. All traces of linolenic or linolic acids had disappeared, but stearic and palmitic acids were still present and could be identified and separated. Some form of an oleic acid was also present.

From the lead and barium salts of the two oils the corresponding acids were obtained in the usual manner.

	Acid from oil insoluble in acetone.	Acid from oil soluble in acetone.
Specific gravity ... Mol. weight in acetic acid)	0·9802 (15° C.) 363—452* (*Sample not completely soluble in light petroleum)	0·9476 (15° C.) 311—344
Iodine value ...... Salts	108—135 Ba and Ag salts insoluble in water; Na salt crystallisable from alcohol Partially reduced to stearic acid by hydrogen and nickel	137—143·6 —
Oxidation products of acids with alkaline permanganate	Traces of dihydroxystearic acid. Some caproic, azelaic, stearic, and palmitic acids, no sativic or linusic acids	13% yield of dihydroxystearic acid. No sativic or linusic acids. The unattacked acid gave a silver salt :— $C_{18}H_{31}(OH)_2O_2Ag.$

The acid from the oil, *insoluble in acetone*, became insoluble in light petroleum when kept in a vacuum. On distillation at 245°—250° C. (44 mm.) about 50% passed over, leaving a dark residue. On redistillation at 225°—230° C. (15 mm. the whole of the first distillate passed over and gave a solid acid (m.p. 31°—32° C.). The iodine value of this acid was 109 and it gave a fluid dibromide (35·1% Br). Analysis of the acid showed it to be $C_{18}H_{32}O_2$ or $C_{18}H_{34}O_2$, with a molecular weight 278 (in glacial acetic acid).

When the acid obtained from the oil, *soluble in acetone*, was distilled, about 50% passed over at 222° C. (20 mm.), leaving a waxy residue soluble in ether, but insoluble in light petroleum and in glacial acetic acid. In benzene solution the residue gave a molecular weight value of 2803 and an iodine value of 118—141. (The molecular weight of oleic acid in benzene is double that of the acid in glacial acetic acid solution). The distillate was fluid and on analysis gave numbers agreeing with the formula, $C_{18}H_{33}O_2$ or $C_{18}H_{34}O_2$. Its molecular weight in glacial acetic acid was 289 and its iodine value 139—140 (unchanged with the time). On reduction with hydrogen and nickel it gave a 78% yield of stearic acid.

From the above facts it is evident that all traces of linolenic and linolic acids have disappeared. Moreover it seems most probable that mixtures of acids are present in the insoluble and soluble forms of the oil, in accordance with Fahrion's view that the oil contains mixed glycerides. It is clear that the acids obtained from the oils are monomolecular rather than dimolecular and that, on distillation polymerisation of part occurs.

The distillates are monomolecular and unpolymerised ; moreover they are more saturated, and the open chain character is shown, in the case of the oil soluble in acetone, by the reduction to stearic acid almost completely. The iodine values, molecular weights, and the general properties of their salts are best explained on the assumption of mixtures of altered (unoxidised but partially polymerised) linolenic, linolic, and oleic acids.

A comparison of the properties of olive oil and heated olive oil showed that the evidence of isomeric change in a non-drying oil was very slight.

In order to throw light on this assumption it was necessary to investigate the methyl esters

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of the thickened linseed oil and to examine the properties of poppyseed oil, because isomerism may occur when this oil is kept at 260° C. for some time.
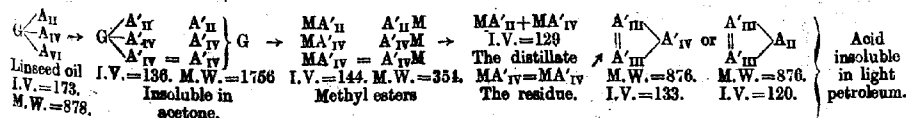
TABLE 3.

Olive oil.

	Raw.	Thickened at 260° C. for 28 hours.
Sp. gr.	0·9154	0·9254
n_D	1·4704 (19° C.)	1·4720 (18° C.)
I.V.	85—94	72·5—85
Lead salt	soluble in ether (8% saturated acids)	soluble in ether (11·3% saturated acids)
Barium salt	74% insoluble in benzol-alcohol	67% insoluble in benzol-alcohol
Barium salt	insoluble in ether	insoluble in ether
Cerium salt	soluble in ether	almost completely soluble in ether
I.V. oleic acid ...	96	92

Methyl esters from thickened linseed oil (*insoluble in acetone*). These were prepared by Bull's method (Ber., 1906, **38**, 3570 ; this J., 1906, 1158) from a linseed oil, insoluble in acetone, which had a molecular weight 1964 and iodine value 130. The methyl esters had the following constants :— Sp. gr., 0·9381 (15° C.) ; r_D 0·3063 (20° C.) ; acidity, 14·2 (*i.e.* 7% free fatty acids) ; iodine value 121·3 (1¼ hours), 163·7 (384 hours) ; [for olive oil the iodine value is 92 (1¼ hours), 86·7 (384 hours)]. Molecular weight in benzene, 362—377 (calculated for a simple ester, 294). The yield was 86% of the theoretical. On distillation about 40% passed over between 200° and 213° C. (15 mm.). The correct boiling point may be considered as between 203° and 210° C. The distillate was colourless and solidified to a waxy solid of m. pt. 7°—9° C. with a specific gravity 0·8936 (15° C.), r_D 0·306 (20° C.) ; molecular refraction, $M_D = 89·9$, and iodine value 131 (1¼ hours) and 131 (72 hours). Molecular weight in benzene, 278 (calculated 294). The methyl ester, distilled as above, was found to contain traces of methyl stearate, which were removed as the acid, and the ester after removal of the saturated acid gave a tribromo-acid. On reduction with hydrogen and colloidal palladium some stearic acid was obtained.

The residue left in the flask had a molecular weight 628 and sp. gr. 0·9725 ; molecular refraction, $M_D = 188·7$, and iodine value 124 rising to 166 in 5 days. This substance was not homogeneous, because 62% was insoluble in light petroleum, and the insoluble part had iodine value 115—184 and a mean molecular weight 870. From it an easily crystallisable sodium salt was prepared, of m. pt. 232° C. (Na 7·6%) with iodine value 120, rising to 181—185 in 6 days (sodium oleate, iodine value 80·3, rising to 86·8 in 6 days).

From the examination of the methyl esters it appears that mixed glycerides must be present in the linseed oil (insoluble in acetone). If linseed oil be assumed to contain glycerides of the acids A_{II}, A_{IV}, A_{VI} (where A is a C_{18} acid combining with 2I, 4I, and 6I, respectively, and the proportions of A_{II}, A_{IV}, A_{VI} are variable and interchangeable between molecules), then the oil insoluble in acetone would consist largely of molecules according to the following scheme :—

$$G\begin{cases}A_{II} \\ A_{IV} \\ A_{VI}\end{cases} \to G\begin{cases}A'_{II} & A'_{II} \\ A'_{IV} & A'_{IV} \\ A'_{IV} = A'_{IV}\end{cases} G \to \begin{matrix}MA'_{II} & A'_{II}M \\ MA'_{IV} & A'_{IV}M \\ MA'_{IV} = A'_{IV}M\end{matrix} \to \begin{matrix}MA'_{II}+MA'_{IV} \\ I.V.=129 \\ \text{The distillate} \\ MA'_{IV}=MA'_{IV} \\ \text{The residue.}\end{matrix}$$

Linseed oil I.V.=136. M.W.=1756 I.V.=144. M.W.=354.
I.V.=173. Insoluble in Methyl esters
M.W.=878. acetone.

$$\begin{matrix}A'_{III} \\ || \\ A'_{III}\end{matrix}\!\!>\!\!A'_{IV} \text{ or } \begin{matrix}A'_{III} \\ || \\ A'_{III}\end{matrix}\!\!>\!\!A_{II}$$

M.W.=876. M.W.=876.
I.V.=133. I.V.=120.

Acid insoluble in light petroleum.

B 2

The proportion of A_{II} present is really much smaller than is given by the above scheme, and it is replaceable by small amounts of stearic and other saturated acids, which will account for their occurrence in the oil insoluble in acetone. It must be noted that the above supposition does not account for 50% of the insoluble modification formed in the thickening. The acids, A'_{II}, A'_{IV}, A'_{VI}, are different, after the thickening, from the ordinary oleic, linolic, and linolenic acids, and there would seem to be good reason for the conclusion that linkage changes have occurred during the thickening and anterior to the polymerisation.

Thickened linseed oil (soluble in acetone). If linseed oil, soluble in acetone, be heated above 260° C. to 292°—315° C., it thickens and about 50% becomes insoluble in that solvent. (The modification originally insoluble in acetone at 260° C., when heated for 5 hours at 293° C., gave nearly 50% insoluble in light petroleum.)

If it be considered that the linolenic glyceride be the first to undergo polymerisation, then it is evident that in the case of the oil, soluble in acetone, the glyceride containing the linolic acid will be the most important factor.

Rollet (Z. Physiolog. Chemie, 1909, 33, 411; this J., 1909, 1209) and other investigators have worked out the properties of linolic acid from the study of the unsaturated acids present in poppyseed oil. It was therefore necessary to examine in detail the changes which poppyseed oil undergoes when heated, and to compare them with those of the thickened linseed oil soluble in acetone. The summary is given in Table 4.
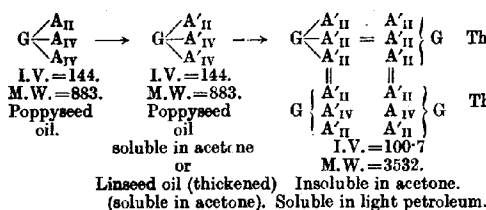
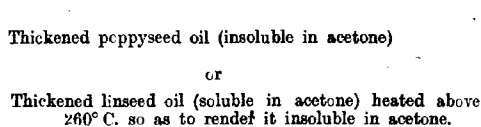iodine value is unchanged, the yield of tetrabromo acid is small and the solubility of its barium salt is altered.

If poppyseed oil, which has been thickened at 260° C., is heated to 290° C., a further comparison with linseed oil (soluble in acetone) can be shown in the following table :—

TABLE 5.

	Poppyseed oil thickened at 270° C. for 28½ hours and at 290° C. for 6 hours.		Linseed oil (soluble in acetone) M.W. 906, I.V. 130—136, heated for 6 hours at 293° C.	
	Soluble in acetone.	Insoluble in acetone.	Soluble in acetone.	Insoluble in acetone.
	40%	50%	46·9%	40·4%
M.W. (in benzene)	989	4054	941	3633
I.V.	97—128	96—134	95—126	104—146
Solubility in light petroleum	soluble	soluble	soluble	soluble

The connection between the two oils is again very close. It has not been possible to obtain a modification from poppyseed oil or from thickened linseed oil (soluble in acetone) insoluble in petroleum, which points to the presence of linolenic acid as necessary for its formation.

The following scheme may represent the changes which poppyseed oil undergoes on heating, and may also with some certainty represent the corresponding changes in linseed oil (soluble in acetone).

$$G\begin{cases}A_{II}\\A_{IV}\\A_{IV}\end{cases} \longrightarrow G\begin{cases}A'_{II}\\A'_{IV}\\A'_{IV}\end{cases} \longrightarrow G\begin{cases}A'_{II} & A'_{II}\\A'_{II} = A'_{II}\\A'_{II} & A'_{II}\end{cases}G$$

I.V. = 144.   I.V. = 144.
M.W. = 883.   M.W. = 883.
Poppyseed oil.   Poppyseed oil
                   soluble in acetone
                   or
Linseed oil (thickened) (soluble in acetone). Soluble in light petroleum.

$$G\begin{cases}A'_{II} & A'_{II}\\A'_{IV} & A_{IV}\\A'_{II} & A'_{II}\end{cases}G$$

I.V. = 100·7.
M.W. = 3532.
Insoluble in acetone.

Thickened poppyseed oil (insoluble in acetone)

or

Thickened linseed oil (soluble in acetone) heated above 260° C. so as to render it insoluble in acetone.

TABLE 4.

	Poppyseed oil.	Poppyseed oil thickened at 260° C. for 28 hours.	Thickened linseed oil (soluble in acetone).
Specific gravity	0·92418 (18°C.)	0·9354 (22° C.)	0·9527 (15° C.)
n_D	1·4737 (20°C.)	1·4792 (22° C.)	1·4846
M.W.	776·6	900—910	900—974
Acidity	32—33	—	8
I.V.	130—136	115—132	92—143
Solubility in acetone	complete	complete	complete
Lead salt	soluble in ether (6·75% saturated acids)	soluble in ether (8% saturated acids)	soluble in ether
Barium salt	soluble in benzol-alcohol, soluble in ether	soluble in benzol-alcohol, 86·2% insoluble in ether	85% soluble in benzol-alcohol, insoluble in ether
I.V. of the acid	126—132	125—132	137—140
M.W. of the acid (in acetic acid)	278	314	311—330
Yield of tetrabromo acid	50%	6%	No crystalline bromo acid

From the above facts it may be concluded that there is a close connection between the properties of the thickened linseed oil (soluble in acetone) and poppyseed oil thickened under the same conditions. It is evident that the linolic acid has undergone some modification, because although the

The above scheme is subject to possible variation in the amount of the acids A_{II} and A_{IV}, and expresses the change in properties of linolic acid (unpolymerised).

In view of the results obtained from the study of poppyseed oil, it may be concluded that linseed oil (thickened and soluble in acetone) contains the components of poppyseed oil, which polymerises only slightly at 250° C., but these components have undergone isomeric change. The chemical properties of thickened linseed oil (soluble in acetone) are similar to, and in some respects identical with, those of heated poppyseed oil under the same conditions. When linseed oil (soluble in acetone) is heated to 290° C., the part which is now insoluble in acetone has the same quadruple molecule as in the case of poppyseed oil.

Tung Oil.

It has been observed that tung oil is easily coagulated by dimethyl sulphate to give a dark coloured solid, which changes its colour to yellow on exposure to air. Moreover, when tung oil is warmed with acetic anhydride and after cooling a few drops of dimethyl sulphate are added, a fugitive, reddish-purple colour is produced which resembles the rosin coloration in the Storch-Liebermann test. The appearance of the colour is accompanied by gelatinisation of the oil. The Storch-Liebermann test with tung oil gives a reddish coloration, which is much less intense

than when dimethyl sulphate is used instead of sulphuric acid. Linseed oil with dimethyl sulphate and acetic anhydride gives a greenish colour.

The above observation may be considered as evidence of the formation of a ring substance before gelatinisation. The investigation of thickened tung oil is in progress, and the results will form the subject of another paper.

SUMMARY.

(1) Linseed and poppyseed oils contain mixed glycerides of variable amounts of unsaturated acids, in addition to small quantities of saturated glycerides, the acids being interchangeable, and their amounts are dependent on the sources and probably on the ripeness of the seed.

(2) Thickening by polymerisation, without change in chemical composition, occurs when there are at least two pairs of doubly linked carbon atoms in the molecules of the acids of the glycerides.

(3) Before polymerisation occurs there is a shifting of the linkages in the molecule, and, in the case of tung oil, there is some slight evidence of ring formation.

(4) The thickening is due to polymerisation of the mixed glycerides, and the first stage is the formation of a product insoluble in acetone, which may be a double molecule of linked glycerides in the case of linseed oil, or a quadruple molecule in poppyseed oil.

(5) The change is dependent on the temperature, and an equilibrium is established when 50% of the modification has been formed.

(6) At higher temperatures the final stage is the formation of a polymer insoluble in light petroleum which seems to be determined in linseed oil by the linolenic acid glyceride.

The author desires to express his thanks to Messrs. Mander Brothers, of Wolverhampton, for permission to publish the results of this investigation.

DISCUSSION.

Mr. F. H. ALCOCK asked what was the cause of the opacity in tung oil varnishes and also of the offensive smell of tung oil ? Had any difference been observed in the behaviour of cold-drawn and hot-drawn linseed oils ?

Mr. COTTERILL inquired as to the method of distinguishing between varying samples in relation to iodine values.

Dr. MORRELL explained that when tung oil was exposed to light it passed into an isomeric modification which was very easily oxidised to a white, insoluble substance. It was the formation of this modification and its subsequent rapid oxidation which was essentially the cause of the opacity of wood oil varnishes. The difference between cold-drawn and hot-drawn linseed oil would be in the amount of mucilage present. The linseed oil and the wood oil used contained no rosin. In the coagulation of wood oil by means of dimethyl sulphate great care must be taken in handling the reagent. Arachis oil had not been investigated. In the hexabromide test for linseed oil the hexa-bromo-acid ought to be separated and its melting point determined. In the determination of the iodine values, all values obtained were compared with a blank determination made with pure olive oil for the same time of contact with the Wijs solution.

Canadian Section.

Meeting held at Toronto on April 16th, 1914.

PROF. J. W. BAIN IN THE CHAIR.

THE MANUFACTURE OF CONDENSED MILK, MILK POWDERS, CASEIN, ETC.

DISCUSSION OF METHODS OF ANALYSIS.

BY R. T. MOHAN, B.A.SC.

As early as 1810 an English Patent was granted to De Heine covering the evaporation of part of the water from milk, and its preservation with cane sugar. Other early English Patents on condensed milk were granted to Newton in 1835, Grimway in 1847, De Lignac in 1847, and in France to Appert in 1827. The first patent for a vacuum pan for evaporating milk was granted, I believe, to Green in England in 1813 (Eng. Pat. 3754).

The object of these early inventors is clearly shown in Newton's English patent No. 6787, 1835, which reads : " For preparing animal milk so that it may be preserved for any length of time with its nutritive properties, and capable of being transported into any climate for domestic and medicinal purposes ; this being effected by adding to the milk a certain amount of sugar, and evaporating it by any suitable means, using only a gentle heat to quicken the operation. It may be brought to the consistency of cream, honey, or soft paste, or even into dry cakes. Cocoa, coffee, or tea may be evaporated with it."

The first instance of the successful manufacture of condensed milk on a commercial scale in America was in 1856 by Gail Borden, founder of the present firm of Bordens (U.S. Patent 15,553 in 1856 ; English Patent 509, 1856). Up to the year 1861 there was little demand for condensed milk, but during the civil war a great demand was created, and from that time on it has steadily increased.

The Anglo-Swiss Condensed Milk Co. was started by U.S. Consul Page, of Zürich, Switzerland, who first made the product in 1865, and in 1866 incorporated the Anglo-Swiss Co., which now produces over 80 per cent. of all the condensed milk manufactured in Australia and Europe.

Milk was first preserved by sterilisation in 1856, and unsweetened concentrated milk, or what is now known as evaporated milk, was first successfully manufactured in Highland, Illinois, in 1885.

The U.S. Census Report of 1909 shows a production of 214,518,310 lb. of sweetened condensed milk, and 280,278,234 lb. unsweetened evaporated milk, increases of 8% and 154% respectively over 1905. The 1913 output in the United States amounted, I am told, to about 250,000,000 cans of sweetened and about 390,000,000 lb. evaporated

The *milk supply* for the condensing must be ample for the factory's capacity, and must be of the highest quality. It is under the rigid inspection of the factory, and constant inspection is also conducted of the herds, pastures, barns, and dairies. Rigid instructions are enforced in regard to cleanliness of the animals and dairies. No feeding or other operation which would raise dust is allowed for one hour previous to milking. Strict instructions are issued against the use of certain foods, such as turnips, garlic, etc., and only limited amounts of ensilage are allowed. Immediately after milking the milk is cooled and aerated by running it over block tin coils through which cold brine or water circulates, and then stored in a cool place till brought to the factory. Each can as

delivered at the factory is opened by the receiver, who is able to detect any undesirable odour in the milk. In addition to the flavour, the temperature is noted. Tests are also made for acidity, any milk above 0·2% being usually refused. As the farmer is usually paid on the basis of percentage of fat, a small sample is taken each day and tested for fat, or sometimes the test is made on a composite sample of a week's delivery, the sample being preserved with mercuric chloride.

It is customary to make frequent bacteriological tests on the supply from each farmer. A good practical test for the number of organisms present in the milk is the reductase test, which is based on the fact that normal cow's milk has the power of decolorising certain dyestuffs, the time of decolorisation (reduction) depending on the number of micro-organisms it contains. The test is conducted as follows:—1 c.c. of methylene blue solution is mixed in a glass tube with 10 c.c. of the milk to be examined, 2 c.c. of paraffin oil is floated over it to exclude air, and the tube is kept at about 115° F. (46° C.). If the dye is decolorised within one hour, the milk is regarded as very bad from a hygienic standpoint ; if decolorised within 3 hours it is of second quality ; if the colour persists for more than 3 hours the milk is good.

Another test depends on the decomposition of hydrogen peroxide by an enzyme present in milk, known as catalase, the catalytic power of which is increased by the bacteria present. This method has not come into general use in Canada.

To determine the nature of the bacteria, so-called "fermentation tests" are applied. The best known of these is the "Wisconsin curd test," in which a pint of milk is heated in a sterilised jar to about 98° F., 10 drops of standard rennet extract is added, and the jar is closed and incubated for about eight hours at 98° to 102° F. The jar is then opened and the odour observed, the curds are cut with a knife, and the appearance is noted. Good clean milk contains practically no organisms but the lactic acid bacteria, which produce no gas and no bad odours, and the curd formed, therefore, should have only an occasional irregular hole. Milk produced under insanitary conditions will produce more or less gas, and the curds will be full of large irregular holes.

Another "fermentation test" is conducted by incubating samples of the milk in sterilised tubes at about 100° F. After twelve hours the samples are examined, and the bacterial content of the milk is judged by the character of the curd, etc.

The milk after weighing is poured through a large strainer and run into large enamelled vats, fitted with stirrers, on the floor below. The room in which these vats are placed is kept as cool as possible. The treatment of the milk from now on depends on the product to be made.

Condensed milk.—The Canadian standard is not less than 28% of milk solids, and not less than 7·7% of milk fat. The last inspection of milk made by the authorities and recorded in Bulletin 257, Inland Revenue Dept., shows that the product on the market complies exceptionally well with this standard.

The fresh milk is drawn from the receiving vats into large copper vats known as fore-warmers, where it is heated after addition of the requisite amount of cane sugar. Some of the fore-warmers are heated by copper jackets, while others depend on live steam from an open pipe ; the latter method introduces some condensed water from the steam, but the amount is very small. The amount of sugar added varies from 16 to 19 lb. to 100 lb. of raw milk. In some cases the sugar is added to the whole quantity of milk before it goes into the pan, whilst in others one-half or three-quarters of the milk is run in, and the sugar added to the remainder. The temperature to which the milk is heated

before it goes to the pan also varies in different factories. These variations by different operators are mainly directed towards overcoming crystallisation in the finished product.

The milk is now sucked into the vacuum pan, and the "condensing" operation begins. The concentration is carried out at a vacuum of about 28 in. and a temperature about 140° F. The vacuum pans used are single type evaporators made of copper, round at each end, with straight sides. They are heated by a steam jacket at the bottom and also internally by large coils, and are connected to a water-jacketed condenser.

The "condensing" takes about two hours. Samples are drawn off at frequent intervals through a double sealed test cup. The consistency is tested by means of hydrometers, the end point being 35° to 36° B. More often, however, the sample is cooled to 70° F., and the appearance and the way the milk "strings" are noted. The operators get quite expert in judging the concentration of condensed milk in this way. As soon as the right consistency is attained, the valves are opened, and the finished product is run into ordinary milk cans (about 14 gallons), which are then placed in a shallow iron tank through which cold water circulates; here they are stirred and cooled, to make the product smooth and free from lumps. The tanks are provided with a series of cam wheels, driven from a central shaft, and so constructed that the milk cans fit rigidly on them. A stationary wooden paddle is placed in each can, and as the cans revolve the milk is stirred and cooled. After cooling, the syrupy product is filled into cans and sealed. This product is not sterilised, preservation being dependent on the low percentage of moisture present and the absence of air in the cans. Table 1 shows the average composition of the product compared with that of other evaporated milks and milk powders. If properly made and kept air-tight, it keeps for several years. It contains too much sugar for use as an infant food.

TABLE 1.

Average composition of condensed milks.

	Solids. %	Ash. %	Fat. %	Protein. %	Lactose. %	Cane sugar. %
Condensed whole milk	72·6	1·6	10·0	8·0	12·0	41·9
Condensed skim milk	70·0	2·0	1·0	10·5	14·5	42·0
Evaporated milk....	26·3	1·6	7·9	7·7	9·1	—
Whole milk powder .	96·3	5·6	26·8	32·0	31·9	—
Skim milk powder ...	91·7	6·9	1·7	33·8	49·5	—

The product obtained as outlined is made from whole milk, and complies with the standard in every way. A skim milk product is also made, but this is always sold as "skim condensed milk." It is manufactured in the same way. (See Table 1 for composition.)

The greatest difficulty in the manufacture of condensed milk is to prevent "sandiness," due to crystallisation of the lactose or cane sugar. A decrease in concentration to prevent this is impossible, as the successful keeping of the product depends on its having less than 30% of moisture, and to effect this the sugar must be added in a proportion to give about 41% cane sugar. Over-concentration and the use of too much sugar increase this sandy condition, but even with proper conditions of amount of sugar and percentage of solids, the lactose generally crystallises. Each manufacturer seems to have his own method of overcoming this, and for this reason practice varies in regard to the method of and time of adding sugar, temperature, etc., in the pan, and the method of cooling.

On opening a can of condensed milk a layer of sugar is often found on the bottom. This may either be lactose which has settled, or cane sugar separated out owing to an excess being used. It is not detrimental to the product, except that the layer of milk above may not have enough solids to preserve it as long as it should be kept.

Another defect in condensed milk is so-called "buttons." On opening a can and pouring out the contents, one or more small lumps, varying in size from a pin-head to a bean, may be found, attached to the side of the can. These are called "buttons," and are not easy to explain. Some state that they are insoluble casein compounds formed by the action of the metals of the tin plate. The peculiar feature, however, is that they appear to grow. A satisfactory explanation for this trouble is yet to be given, I believe.

Occasionally a can of milk is found to be in a thick, gelatinous condition. This denotes too much milk solids and not enough cane sugar to make a syrup.

Other defects are rancidity, brown colour, blown tins, or putrid odour. These conditions are due to too low percentage of solids to prevent bacterial changes, but at most they are rarely very marked until the milk is from 2 to 4 years old.

Thus it is seen that the manufacturer is faced with a difficulty as regards this product. Too little sugar may result in a gelatinous product or one that will not keep, whilst too much may cause excessive "sandiness" and separation.

Evaporated milk in Canada is defined as milk from which a considerable portion of water has been evaporated, and contains not less than 26 % of milk solids, and not less than 7·2 % of milk fat. This product therefore does not contain any added sugar, and is preserved by sterilisation.

The milk is drawn from the receiving tanks into the fore-warmers as before. Here it is brought to a boil, and then drawn into the pan and condensed as before, the operator drawing off an occasional sample, and testing the solids by hydrometer; when the proper density is reached the valves are opened, and the milk is run over a series of cooling coils to prevent any rapid multiplication of organisms. From the coolers the milk runs into large copper vats, and a sample is tested for fat and solids. If these tests are satisfactory, the milk is next homogenised by breaking up the fat globules into very minute particles, and mixing them so intimately with the caseous matter of the milk that the cream does not rise to the top. It is claimed that homogenising makes the milk more digestible. This process is accomplished by heating the milk to about 185° F., and forcing it through fine metal capillary tubes under a pressure of about 250 atmospheres against a conical surface of agate or metal. Homogenised milk cannot be separated by means of a separator. From the homogeniser the milk goes to the filling machines, where it is run into cans, which are sealed and transferred to the steriliser. The sterilisers are large circular iron drums, with a revolving framework inside. The cans, in crates, are placed in compartments of the revolving framework. When filled, the door is closed, the retort nearly filled with water, and the temperature raised to the desired point and maintained for the necessary time, the can revolving all the time. The steam is then turned off, and cold water run in till the cans are cold. The time and temperature are very important, and are very variable, so that this part of the work is in charge of experts. The factors governing the sterilisation are acidity, solids, fat content, the season of the year, and size of cans. Milk of high acidity (over 0·4 %) will easily curdle with high temperature, hence the reason for keeping the acidity as low as possible on the fresh supply. The effect of acidity on the milk is shown by Table 2

made from actual experiment. The same milk was used in each instance, and the same temperature and time.

TABLE 2.

Effect of increased acidity on milk. Fresh milk 0·17 % lactic acid.

Concentration.	Acidity.	Condition of milk.
1·58 : 1	0·30	Not precipitated
1·74 : 1	0·34	,, ,,
1·90 : 1	0·40	,, ,,
1·99 : 1	0·43	,, ,,
2·11 : 1	0·48	Small lumps of curd
2·25 : 1	0·54	Large ,, ,,

NOTE.—Chemical changes during concentration and sterilisation apparently affect the acidity.

Milk of different seasons will stand different temperatures, fortunately the highest in the summer. The fresh milk varies in composition with the seasons, and hence the concentration also has to be varied to bring the product up to standard. Table 3 illustrates this :—

TABLE 3.

Variation in concentration with seasons.

	Solids in fresh milk.	Concen- tration.	Solids in condensed milk.	Condition of condensed milk.
June	12·68	2·00 : 1	25·38	Smooth, no
August	11·75	2·21 : 1	26·01	separation or
November	13·40	1·99 : 1	26·62	curdiness.

NOTE.—Lower concentration causes separation of fat, and higher causes curdy milk.

In most factories it is customary to make a trial sterilisation on a small batch to see what temperature the milk will stand before it curdles. To do this a small steriliser is built on the same plan as the large one, and holding half a dozen cans. The milk is sterilised at 235° to 240° F. (113°—116° C.) for about 30 minutes. The milk is next shaken to make it smooth and uniform. About 4 dozen cans are fitted into crates, and placed in a machine which has a very rapid oscillating motion for one to three minutes, depending on the milk. After shaking, the milk is stored in a warm place (practically a large incubator) for about three weeks prior to shipping. Any "leaks" or "swells" are then picked out, and the good cans are labelled, cased, and shipped.

This, therefore, is a product which is desirable from every standpoint, handled under sanitary conditions, and completely sterilised. It is a concentrated whole milk product containing no adulterants, and finds a ready use for general and for infant feeding.

Absolute cleanliness is maintained in the factories. All pipes are cleansed daily with hot soda solution and then with live steam, and the vats, coolers, and vacuum pans are scalded, scrubbed, and sand-papered every day.

Defects.—Swells, flat sours, and sweet curdling in evaporated milk are due to under-sterilisation. Curdiness (other than sour curd) is due to precipitation of the curd as a hard mass under the action of the heat on a product of high solids and acidity. The hard grains sometimes found in the bottom of the cans consist of mineral matter, mostly calcium phosphate, precipitated owing to over-concentration.

Plain condensed milk is milk evaporated about 4 : 1, which is filled into barrels, and used within a day or so by ice cream manufacturers and confectioners.

Analysis of condensed milk.

Sampling.—In the evaporated or unsweetened variety there is little difficulty in getting an uniform sample from the can, as it is only necessary to stir it thoroughly. However, the condensed or sweetened variety presents a possibility of error, especially when the sugar has settled. The best method of sampling in this case is to transfer the whole contents of the can to a large mortar, and thoroughly grind and mix it ; a 40% solution is then prepared and analysed.

Solids.—For the sweetened condensed milk a quantity of the 40% solution is evaporated to dryness, *in vacuo*, or in a McGill oven (in which the product is dried in a current of air at 70° C.). Drying to a constant weight on a steam bath or in an ordinary air oven does not ensure accurate results, as the solids seem to retain a small proportion of the moisture with great tenacity, and if dried too long undergo chemical changes.

For the unsweetened or evaporated milk two methods are available, one by taking the specific gravity of the 40% solution and calculating the solids by formula, the other by evaporation and weighing. For taking the gravity hydrometers with special scales, called lactometers, are used. The two most common are the New York Board of Health and the Quevenne lactometers. In Canada the former is used almost entirely. The formula used to calculate the solids is :—
$$S = 1.2F + 0.25 (G—1000) + 0.14,$$ where S is the percentage of solids, F the fat, and G the specific gravity referred to water as 1000.

This gives good results, but only providing the fat has been determined accurately. It is obvious, therefore, that this method cannot be relied on entirely, and a quantity of the milk must be dried *in vacuo* and the residue weighed.

Ash is determined by burning the residue after evaporating the milk for solids. A temperature sufficiently high to volatilise the chlorides must be avoided.

Protein is determined by the usual Kjeldahl method. The conversion factor is somewhere between 6·25 and 7·04. Provisionally the factor 6·38 is used.

Sugar.—In evaporated milk the only sugar present is lactose, and this is determined either by the polarimeter or by the gravimetric Fehling process.

In the condensed milk there is, in addition to the lactose, a large percentage of cane sugar, and accurate results are difficult, co-operative work by the U.S. Association of Agricultural Chemists on the same samples having shown results for lactose varying from 9·74% to 12·05%, and for cane sugar from 43·06% to 46·74%.

The author has had a batch of milk prepared specially, and from the weight before and after concentration calculated what the composition of the finished product should be ; invariably analysis showed a little more lactose and a little less cane sugar than there should be. It was thought possible that in the concentration there was a slight inversion of the cane sugar, making it appear to be lactose, but from experiments on mixtures of cane sugar and lactose under similar conditions, it is certain that no change takes place.

Fat.—The determination of fat is by far the most important of all, and it is most difficult to get accurate and concordant results.

Table 4 will show some results obtained by different methods. These results only deal with evaporated milk, as the condensed milk requires different treatment.

TABLE 4.

Determinations in Fat by Different Methods.

Calculated fat.	Babcock.	Ether extraction.	Rose-Gottlieb.
%	%	%	%
7·25	6·9	6·83	6·87
7·98	7·7	7·46	7·78
8·74	8·1	8·13	8·26
9·14	8·7	8·33	8·90
9·70	9·1	8·67	9·40
10·35	10·3	9·13	10·07
Average 8·86	8·46	8·09	8·55

The most reliable of these methods is the Rose-Gottlieb, but this averages 0·31% fat low. The reason for these differences lies in the physical change which the milk has undergone during the concentration, homogenising, and the sterilisation. The casein has been invisibly precipitated into an insoluble curd, and each very minute particle of precipitated casein encloses a small amount of fat. In order, therefore, to extract all the fat it is necessary to dissolve completely the curd and liberate the fat. To this end many modifications and new methods have been proposed. With one or two exceptions these are not feasible.

In the ordinary Babcock method it is almost impossible to get a clear fat column; the acid appears to char the milk to a greater or less extent, depending on the concentration, season of the year, etc. The only rapid and accurate modification known to me is as follows :—4·5 grms. of the milk is accurately weighed into an ordinary Babcock test bottle, 17·5 c.c. of water added, and thoroughly mixed. Then 17·5 c.c. of concentrated sulphuric acid is added and mixed to dissolve the curd completely, and the mixture is centrifuged for five minutes. The bottles are filled to the neck with hot half-strength sulphuric acid, centrifuged again for 2 minutes, filled to the top of the graduations with boiling water, centrifuged for 1 minute, and the fat column read at 185° F. This reading multiplied by four gives the percentage of fat in the evaporated milk. The important points to be observed in this method to obtain a clear fat column and complete recovery of the fat, are correct dilution of the milk (4 : 1) before adding the strong acid, and the addition of hot half-strength acid in place of water after the first centrifuging.

TABLE 5.

Fat by modified methods.

Calculated fat.	Modified ether extraction.	Modified Babcock.
7·25	7·20	7·30
7·98	8·00	7·98
8·74	8·75	8·68
9·14	9·20	9·20
9·70	9·65	9·60
10·35	10·40	10·40
Average 8·86	8·86	8·86

In the gravimetric methods it is also necessary first to remove the caseous matter, and then extract the fat. This is best done by the following method. A weighed amount of the evaporated milk diluted 4 : 1 is absorbed on a filter coil free from fat, placed in an extraction cone, and without any preliminary drying extracted in a Soxhlet apparatus with 1% acetic acid for two hours. This removes most of the protein matter. The cone is washed with hot

water to remove the acetic acid, dried in an air oven at 100° C. for six or eight hours, and extracted for eight hours with ether in the ordinary way, and the extracted fat weighed.

The reliability of these modified methods is shown in Table 5.

In determining the fat in condensed milk there is an added difficulty of the presence of cane sugar. For gravimetric estimation the modified ether extraction method described above is to be recommended. For a rapid centrifugal method, the following modification (by Leach) gives fair results : 15 c.c. of the 40% solution of condensed milk is measured into a Babcock bottle, and enough of a copper sulphate solution is added to precipitate the proteins. The bottle is then centrifuged, and the precipitated proteins carry the fat to the bottom of the bottle. The clear liquid above is then drawn off by means of a pipette having a wisp of cotton wool over the end to prevent any of the precipitate being withdrawn, and the remaining fat and protein is thoroughly mixed with water and again centrifuged. This operation is repeated until the sugar has all been removed. 17·5 c.c. of water is added to the precipitate, then 17·5 c.c. of strong sulphuric acid, and the operation continued as in the ordinary Babcock test. This method eliminates the trouble due to charring of the sugar, but still has the defects connected with the Babcock test when used for evaporated milk.

Milk powders.—In making these the difficulty has been to produce a powder which when mixed with water would produce a fluid similar to milk in appearance, flavour, and physical properties. Many methods have been tried, and numerous patents granted, but, with one or two exceptions, there has been little success. The two most successful processes are by drying on steam-heated rolls, and by spraying the milk into a tower.

In the roller system, the milk is run on to steam-heated metal rolls, generally *in vacuo.* The dried powder is scraped off the rolls, and ground. The resultant powder, while fairly good, is not as soluble as it should be.

The spraying system has been more successful. The milk is first reduced in a vacuum pan to about one-fifth of its volume. It is then atomised into the top of a hot chamber, the moisture being removed while the fine particles of milk are falling to the floor. The dried product accumulates on the floor as a very dry flour, and needs no grinding. The powders produced by these spraying systems are excellent, and find a ready use with bakers, confectioners, etc. For composition see Table 1.

These products are analysed by making a solution the strength of ordinary milk, and analysing this. All the difficulties mentioned for the analysis of evaporated milk are also met with in this product.

Casein.—When the milk supply is too heavy to be handled by the evaporators, it is usual to skim the milk, ship the cream in to the cities, and prepare casein from the skim milk. The present uses of casein are numerous and increasing. They include paints, dressing for textiles, cements and mucilages, plastic masses, sizing for paper, food products (under trade names such as Sanatogen), and many others.

The casein content of ordinary cow's milk averages 3·2%. It is easily precipitated by acids. Technically, it may be made by spontaneous souring of the milk, or more often by the addition of acids, as hydrochloric, sulphuric, or acetic acid ; also by precipitation by rennet. Combinations of these methods are also used, the casein being sometimes dissolved in alkali and re-precipitated by another acid. Many patents cover the manufacture of this product, each one of which has its own special claims. The casein is washed and dried on trays, preferably in a vacuum drier. It is then ground.

The trade in America is controlled by two companies, the Union Casein Company and the Casein Company of America, both of which manufacture many products from the raw material.

Those specially interested in casein and its compounds are referred to Robert Scherer's book on " Casein : Its Preparation and Technical Utilisation."

Not infrequently the whey (after the separation of the casein by rennet) is evaporated down, and the lactose obtained. Processes similar to the manufacture of ordinary sugar are used.

London Section.

Meeting held at the Northampton Institute, Clerkenwell, on Monday, January 4th, 1915.

PROF. W. R. HODGKINSON IN THE CHAIR.

PRODUCTION OF NITRATES FROM AIR, WITH SPECIAL REFERENCE TO A NEW ELECTRIC FURNACE.

BY E. KILBURN SCOTT, A.M.INST.C.E., M.I.E.E.

In papers on the " manufacture of nitrates from the atmosphere " read before the British Association, in August, 1911, and before the Royal Society of Arts, in May, 1912, I pointed out that we were entirely dependent upon raw material from oversea from which to make explosives, and in case of war might be in a serious position, and I urged the necessity of starting the production in this country of nitrates from air by electricity.

Messrs. A. McDougall and F. Howles, of Manchester, first made nitric acid from the air in a practical way about a dozen years ago, but Norway has the honour of making the process a commercial success, Professor Birkeland and Dr. S. Eyde being principally responsible.

Although the first installation in Norway of about 160 horse-power was only started about ten years ago, the business has gone ahead with such leaps and bounds that nearly a quarter of a million horse-power is employed for making nitric acid from the air, in that country alone. Some of the furnaces take over 4000 H.P., and one factory absorbs 140,000 H.P., whilst another of 120,000 H.P. is being built.

For several years I have been at work on the problem of evolving a new furnace to work with three-phase alternating current, also a system of working a complete plant with a view to obtaining better yields than are obtained by the present single-phase furnace plants abroad. I propose to give some particulars of the furnace and method of working.

All nitrogen fixation furnaces have electrodes of metal between which alternating current arcs are formed. These arcs are " blown " into flames by a magnetic field or an air blast, and provision is made for the passage of large quantities of air through these flames.

Owing to the great heat of the electric arc, and possibly also to electronisation, some of the air is acted upon and the nitrogen and oxygen combine to form nitric oxide. As this gas dissociates unless it is immediately cooled, it is necessary to provide a cooling zone in close proximity to the flames and arrange for the gas to enter that as quickly as possible.

The principal points to be considered in the design of a furnace are :—

First. To ensure that as much of the air as possible is brought into contact with the arc flames.

Second. To remove quickly and cool the fixed gas.

Third. To dispose the electrodes so as to minimise adjustment and renewals.

Fourth. To provide automatic regulation of current and continuity of working.

Before proceeding to describe my own furnace it will be an advantage to describe briefly those in use abroad.

The Birkeland-Eyde Furnace.

The best-known furnace is that due to Birkeland and Eyde. At the Notodden works in Norway there are 32 of them of 600 to 1000 K.W. each, and at the Saaheim works there are 8 of 3500 K.W. each. The furnace consists

naces are connected in delta as shown in Fig. 2. The full voltage between phases is available at the terminals of each furnace, and at Notodden this is 5500 and at Saaheim 11,000 volts.

A peculiar feature of the arc flames of this furnace is that in moving along the electrodes they do not do so concentrically but somewhat as shown by the circular broken lines indicated diagrammatically in Fig. 1B.

FIG. 1A.　　　　　　　　　FIG. 1B.

Birkeland-Eyde single-phase furnace with magnetic field for blowing the arc flame.

of steel castings built up as shown in Fig. 1A and having between them a cylindrical structure of firebrick, shown in black, with a disc-shaped chamber in the centre. Air enters by a pipe at the base of the furnace and passes into the central chamber by means of a large number of small holes. After flowing radially through the central reaction chamber it collects in a circular channel just inside the periphery of the furnace and passes to the outlet pipe and away. Two U-shaped electrodes project horizontally into the disc chamber from each side, as shown in Fig. 1B. They are made of copper tubes 1¼ in. diam. and about ⅛ in. thick, and the total length of each tube before being bent into shape is about 20 feet. Each electrode is adjustable vertically and sideways. Arcing tips of copper are attached to the rounded ends of each tube, and these tips are spaced about one-third of an inch apart when in the normal position. Cold water circulates through each electrode in insulated pipes, as indicated by the arrows in Fig. 1B.

It is a peculiarity of this furnace that both alternating current and direct current are used. The former is for the arc and the latter for the powerful electric magnet, the north and south poles of which are shown, in Fig. 1A, embedded in the firebrick lining. The direct current supply is indicated at the top of Fig. 1A, and the alternating current single-phase supply at top of Fig. 1B.

The magnetic field is at right angles to the electrodes, and consequently, when alternating currents flow, the magnetic field blows or deflects the arcs outwards into the disc-like chamber. As each electrode is alternately positive and negative, the arc flames are projected rapidly first to one side and then to the other, so that to the eye there appears to be a constant circular sheet of flame. In the 1000 K.W. furnaces the flame is about 6¼ ft. diameter and in the 3500 K.W. furnaces 8 ft. diameter. The pole faces are about 25 cm. apart, and the magnetic field is about 5000 C.G.S. lines per sq. cm., consequently very large magnetising coils are necessary, and about 10% of the total energy is required to excite them.

It should be especially noted that this furnace works with *single*-phase alternating current, and therefore on a three-phase circuit the furnaces must be used in sets of three. The design is such that it is not possible to utilise all the three phases in a single furnace. The three fur-

As the cooling air is the controlling factor it is not possible to preheat that which enters the arc flame at the centre.

At the International Congress of Applied Chemistry in 1912 Dr. Samuel Eyde gave the temperature of the flames as 2500° C. to 3000° C., and the temperature of the escaping gases between 800° and 1000° C. He also stated that the most exposed parts of the electrodes require to be changed every third or fourth week and the lining every fourth to sixth month. Each of the furnaces at Saaheim is said to take just under 2000 cub. feet of air per minute.
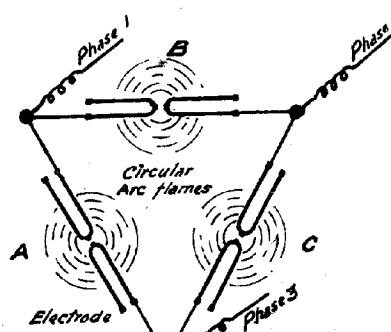

FIG. 2.

Three Birkeland-Eyde furnaces connected in delta.

The Schönherr-Hessberger Furnace.

This furnace is used at the Christiansand works of the Badische Anilin und Soda Fabrik, where there are 12 furnaces of 450 K.W. each; at the Saaheim works there are 96 of 1000 K.W. each.

The apparatus consists of four annular steel tubes arranged vertically as shown in Fig. 3. The outer tube is about 3 feet diameter, is made of plates riveted together, and is lined with firebrick. The innermost tube, about 5 in. diameter, forms the reaction chamber, and up the centre a standing arc flame is maintained by means of a
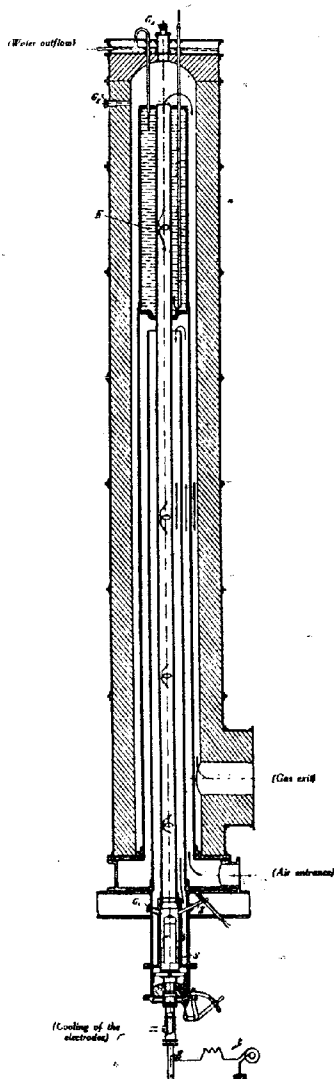

FIG. 3.
Schönherr-Hessberger single-phase furnace, with combined preheater.

whirling current of air. The air inlet and outlet tubes are so arranged that outgoing hot gases preheat the incoming air as indicated by the arrows in Fig. 3. It is therefore a furnace and a preheater combined. By means of a number of tangentially arranged air inlets at the bottom of the reaction tube, the air is given a whirling motion, which helps to keep the arc flame in the centre of the tube. The pressure of the air at the bottom is equal to 50 to 100 cm. of water.

The bottom electrode consists of an iron rod insulated from the furnace. It passes through a water-cooled copper gland, and as it burns away is pushed upwards, fresh rods being screwed on as required to give continuity of working.

The arc is started by means of a lever (marked Z in Fig. 3), which is momentarily placed between the bottom electrode and the reaction tube, the latter being of course at earth potential. The whirling air current then extends the arc upwards to a water-cooled electrode, K, at the top. The top of the arc plays about inside this electrode, and pits the surface.

Some of the air comes in contact with the arc flame and is converted into nitric oxide, and at the top, where the arc strikes from the centre to the side, the fixed gas mixes with the rest of the air that is whirling past. This and the water jacket of the electrode act as the cooling zone. Experience has shown that good yields of gas can be obtained when the air travels parallel to the arc. The furnaces are connected in star as shown in Fig. 4.
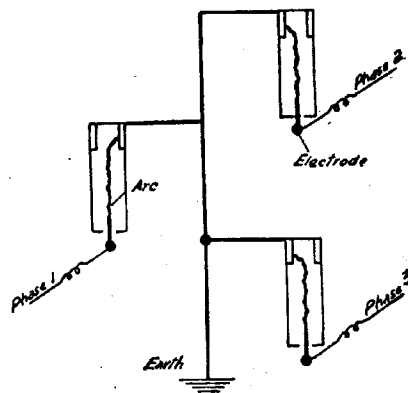

FIG. 4.
Three Schönherr-Hessberger furnaces connected in star.

Although claims for three-phase working are made in the Schönherr patent and three arc flames are shown inside one tube, they could not work that way, as they would collapse together. Also it would be impossible to have three separate whirling air currents in one tube.

As compared with the Birkeland-Eyde furnace, the Schönherr-Hessberger has the advantage of using only one kind of electric current, and there is thus less electrical gear. Other things being equal the energy required for a given output of gas should be less, and in actual practice this appears to be the case.

The 450 K.W. furnaces at Christiansand have standing arcs about 15 feet long and the 1000 K.W. furnaces at Saaheim have arcs about 20 feet long. This makes the furnaces very long and difficult to repair, e.g., those at Saaheim are about 40 feet high.

The relatively great height of the furnace, combined with the difficulty of maintaining so long an arc, presents considerable mechanical and electrical difficulties in building for large powers. That is partly why the furnaces at Saaheim are only for 1000 K.W., whilst the Birkeland-Eyde furnaces are of 3500 K.W.

This question of the limiting size of furnace is important because it would appear that the larger the furnaces the better the yield for a given amount of electrical energy and for a given expenditure in furnace plant. This is always the case when radiation losses form a large part of the total power.

The Pauling Furnace.

The Pauling furnace is used in nitric acid factories at Gelsenkirchen, Innsbruck, and Milan, also at Roche de Rame, France, and in South Carolina, U.S.A.

The furnace is built on the lines of a horn type arrester—that is to say, it has two electrodes which diverge so as to give a fan-shaped space between them, and has an air blast which fills the fan-shaped space with flame, as shown diagrammatically in Fig. 5.
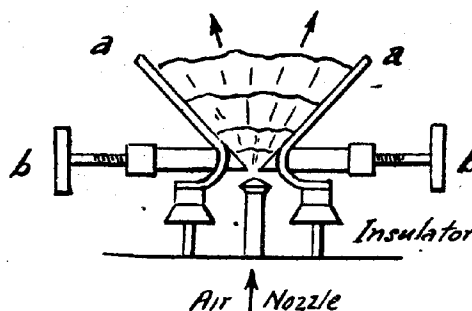

FIG. 5.

Diagram of the Pauling single-phase furnace.

To get the continuous blown arc flame it is necessary first of all to set the electrodes at such a distance apart that the applied voltage will easily jump across, and, second, to blow air between the electrodes so that directly an arc is struck it is immediately forced upwards and goes out, to be followed by others at each half-cycle of the alternating current. There is a separate Pauling furnace to each phase and each has two pairs of electrodes connected in series. There are ducts for the supply of air and a chimney at the top to carry off the gases. Two separate supplies of air are provided; one is preheated and goes to the bottom of each set of electrodes, and the other, which is for cooling purposes, strikes into the top of the arc flames. The velocity of the cooling blast may be less than the other, so as to mushroom out the flames at the top to facilitate cooling.

In order not to dilute the newly-fixed gas the cooling blast consists of some of the air and fixed gas which has passed through the furnace and been cooled down.

The electrodes are of cast steel piping and each is in three pieces, so that the enclosed portion can be reversed when it is burnt or fritted. The electrodes are set several inches apart to allow the air supply to pass through, and from each electrode there projects a starting or kindling blade of thin copper set on edge so as to obstruct the air as little as possible. These kindling blades are approached to within about 3 millimetres of each other, and as they burn away are fed forward. They pass through the bottom horizontal bar of the main electrode. Each main electrode is carried on a triangular frame by insulators, and adjusting screws are provided to set it accurately.

The two pairs of electrodes are in series and the middle point is connected up to a high resistance in such a way as to bring a high voltage to bear on the gap between one pair of electrodes. This establishes the arc, and the tension at that point then sinks so that nearly full pressure is available for the other pair of electrodes. In this way a pressure nearly as high as that available for kindling the first arc is now active in kindling the second one, and in the instant when the latter is formed the circuit is completed through the two arc flames.

Although the Pauling furnaces at present in use are smaller than those employed in Norway, the design is such that there are no physical limitations as to size and he-ght, etc. The structure of the furnace is simple as compared with the furnaces used in Norway, and repairs can be carried out easily. The air passes straight through the furnace without any devious or throttled passages.

Comparison of above furnaces.

Comparing the above it will be seen that the furnaces are of three distinct types, as follows:—
The Birkeland-Eyde is a *Magnetically Blown Arc Furnace;* the Schönherr-Hessberger is *A Long Standing Arc Furnace;* and the Pauling is an *Air Blown Arc Furnace.*

Each furnace is supplied with single-phase alternating current and the first two have single arc flames, whilst the Pauling has two separate arcs in series on a three-phase supply. All the types of furnaces are therefore worked in sets of three.

In the first and the last types the cooling is effected by blowing cool air into the top of the arc flame, whereas in the Schönherr-Hessberger furnace the only air which passes is that previously preheated in the furnace itself.

The Birkeland has the disadvantage that it is necessary to use direct current as well as alternating current. This not only uses up a considerable amount of electric energy but necessitates additional apparatus. Blown arc flames can be obtained just as effectively by an air blast.

From the standpoint of accessibility, the design of the Schönherr-Hessberger is perhaps most at fault, and its great height makes it difficult to construct for large powers. It is the only one with a combined preheater, but there is no advantage in this. For example at Saaheim there are 96 preheaters, whereas two or three separate ones would preheat all the air for the 96 furnaces more effectually and be very much cheaper.

The Birkeland-Eyde furnace has the most complicated refractory lining, and it is in close proximity to the arc flame it is expensive to maintain. The throttled and devious nature of the air path through the furnace requires considerable power to circulate the air, and it should be noted that when comparing various designs, it is necessary to take all the power into account.

When connected on a three-phase supply, three Birkeland-Eyde furnaces require six high tension electrodes, whereas three Schönherr-Hessberger furnaces require only three high tension electrodes, the other three being at earth potential. On the other hand three Pauling furnaces require no less than twelve high tension electrodes.

The electrodes of the Schönherr-Hessberger furnace are simpler and cheaper than those of the Birkeland-Eyde, which being of copper are expensive to renew. The electrodes of the Pauling furnace are complicated by reason of the copper kindling blades which require adjustment and renewal. There is also a possibility of water leaking from the joints.

Experimental apparatus.

Considering the universality of three-phase apparatus it is rather surprising that those interested in nitrogen fixation factories abroad should have kept to single-phase designs. It may be due to patent and royalty considerations and absence of competitive conditions.

In some respects the present position is somewhat similar to that which obtained when three-phase alternators first came to the front. Until then single-phase had always been used, but very soon single-phase designs went out of use. Three-phase supply is now practically universal. When I commenced to develop a new design of nitrogen fixation furnace I decided that the proper thing to do was to choose such a method of producing the arc flames that the furnace could be constructed as a self-contained three-phase unit having only three electrodes.

Until I had actually demonstrated my three-phase furnace at work there were several who anticipated difficulties in starting three arcs, also trouble from unequal burning away of electrodes, unequal balancing, etc. Experience has shown conclusively that none of these difficulties exists. The furnace works much better and steadier than a single-phase furnace, and this has been remarked upon by several who have seen both types at work.

When current has to be taken from a general power supply the importance of having a three-phase furnace cannot be over-estimated.

In such negotiations as I have had for a supply of electric energy, I have generally been asked whether the load would be balanced and what were the chances of continuity of working.

When a company owns its own water power, as in Norway, and has plenty to spare, with no other consumers to consider, then such questions as maintaining a balanced and a constant load on all three phases is not so important.

Fig. 6 shows the lay out of my experimental plant as fitted up at the Northampton Polytechnic Institute, Clerkenwell (by permission of Dr. Mullineux Walmsley).

closed, a stream of high tension sparks immediately jumps across from the wire to the electrodes. The air dielectric being thus broken down, the main three-phase current can then follow. These two electrical circuits do not interfere with each other.

The bottom ends of the main electrodes are set far enough apart to allow the air to pass freely, and they do not require any adjustment because the pilot sparks always make a path for the main current to get across.

The operation of starting up the furnace is very simple. First turn on the air blast, then close the isolating switch
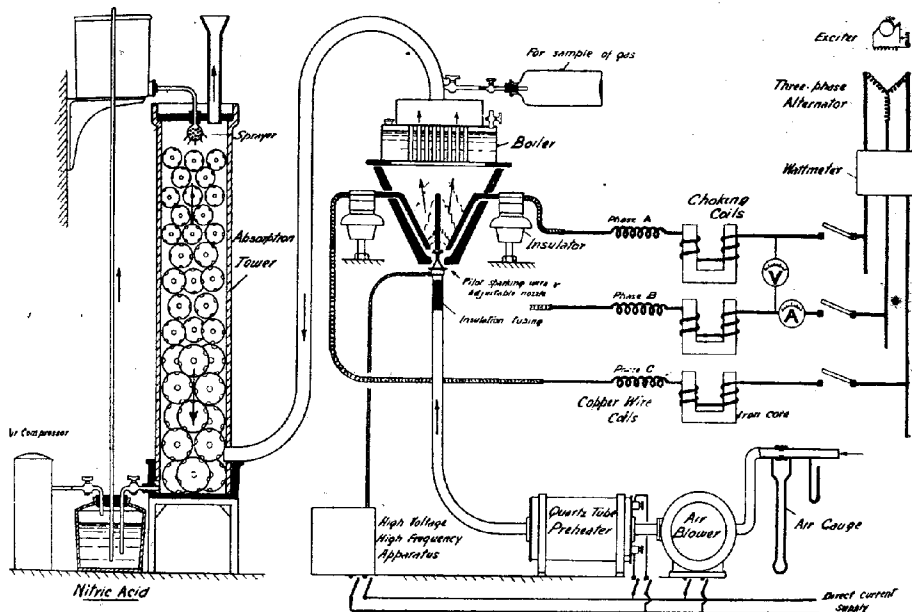

FIG. 6
Experimental Apparatus.

Three-phase current at 2000 volts, 25 periods, supplied from the power house of the Institute passes via a watt meter and three-pole isolating switch to two sets of choking coils. The first has U-shaped laminated cores, and it is possible to regulate the choking effect by connecting more or less coils in series. The second consists of insulated tubes on which a single layer of wire is wound. These latter are to take care of sudden rises of pressure. The proper proportioning of the choking effect is a most important factor, a point which I early appreciated when assisting Mr. Howles in nitrogen fixation experiments about 14 years ago.

The three electrodes of the furnace are attached to double petticoat porcelain insulators spaced 120° apart, two of which are shown in the centre of Fig. 6. The electrodes are of steel, and the inclined sides are bent at about 30° from the vertical line. A standard fireclay crucible serves as the wall of the furnace. The bottom of the crucible is drilled through, and immediately beneath is the air-supply pipe, the nozzle of which consists of an iris diaphragm.

The upper portion of the pipe is made of insulation material and a No. 18 gauge iron wire is attached to the nozzle so as to project vertically upwards with its point midway between the three electrodes and just below them. This wire is for the pilot sparks and it is connected to a high frequency high voltage apparatus somewhat similar to apparatus used in wireless working.

Current from an ordinary lamp pendant supplies the apparatus, and when the tumler switch of this circuit is

so as to make the electrodes alive and finally close the tumler switch of the high frequency set. Directly this is done the sparks jump from the wire to the electrodes and the three-phase arc flames are started. To stop the furnace, the tumler switch is switched off and the arc flames then stop.

Air is supplied by an electrically driven blower, and it is measured by a manometer as indicated at the right-hand bottom corner of Fig. 6. It is only necessary to measure the difference in height of liquid in the U-tube, and then by means of a formula the amount of air is quickly calculated. The method is much more handy and cheaper than a meter; besides, with a wet meter the air may take up moisture.

The three phases working together give a combined flame of more or less inverted cone shape. The air enters this and blows the arc flames up to a point at the top which flickers about like an ordinary flame.

On top of the furnace (in fact the roof) is a boiler with vertical copper tubes for the gases to pass through. The position of the boiler can be adjusted vertically. It is, of course, connected to earth. As the peak of the arc flame is the neutral point of the three-phase supply it does not matter if it strikes on to the bottom of the boiler. As a matter of fact during the experiments I have frequently placed the boiler so low as to cut off a considerable portion of the upper zone of flame. Although the tubes are only soldered into thin tinplate, there was no difficulty in doing this, for the steam raised in the boiler carries off the heat very rapidly.

In the pipe leading from the boiler a cock is provided to allow of the gas being drawn into glass bottles from which the air has been exhausted. This is the usual method of testing.

a cross-section through the boiler. The construction of the electrode should be noted. It consists of a steel tube divided longitudinally into two parts so that the cooling water travels down one side and up the other.
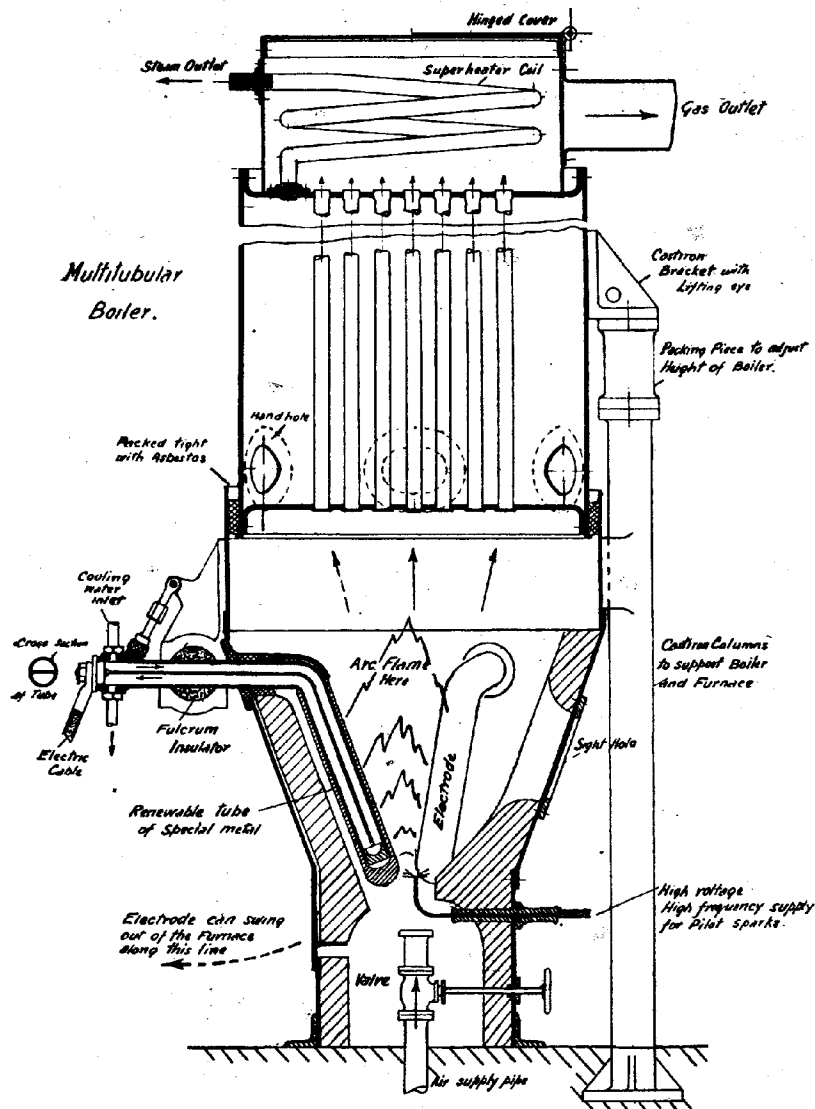

FIG. 7.

Kilburn-Scott three-phase furnace for fixation of nitrogen

For the purpose of absorbing the gases an earthenware pipe filled with Guttman hollow balls is provided. See left of Fig. 6. Water trickling down meets the gas going up, and so forms nitric acid which collects at the bottom. The liquid can be raised by compressed air and so passed through several times.

Kilburn-Scott Three-phase Furnace.

Fig. 7 shows my design of a full-sized commercial furnace and Fig. 8 shows the plan of the three electrodes and also

A renewable tube of cast steel is slipped over the cooling tube from the bottom, and when one side of it is burnt or pitted by the arc flames it can be turned round to present a new surface. The turning can be done in a few minutes. This form of electrode has the advantage of giving minimum insulation where it passes through the furnace wall, for if there were horizontal limbs top and bottom both these would have to be insulated. Also by dispensing with a horizontal bar at the bottom it is much easier to arrange for the pilot sparking conductor and the air

supply. The electrode swings from a large insulator at the outer end of the horizontal limb, so that the electrode can be quickly swung out of the furnace and also swung back again with the certainty of returning to its correct position. The pilot sparking conductor passes through a porcelain insulator fixed in the wall of the furnace below the electrodes, which part of the furnace is of course comparatively cool.

The boiler is carried by three cast iron columns which are at 120 degrees apart and set between the three electrodes. Space for adjustment is provided between the furnace and the boiler, so that the height of the boiler above the electrodes can be varied to suit the size of the arc flames and the velocity of the air. The bulk of the brickwork is remote from the arc flames, so that ordinary plain fire-bricks can be used. As all brickwork and refractory material is porous to a certain extent, the whole is enclosed with thin steel plates which are electrically "earthed" and sectionised.

Three arcs together help to maintain each other because current is always flowing in one or other of the phases. Thus continuity of working is assured and the load is always balanced. When current is purchased from a power station these are most important matters.

By breaking down the air dielectric with high frequency pilot sparks, the arcs start directly the zero points of the alternating current waves are crossed and this improves the efficiency and power factor. There are no kindling knives to burn away and get in the way of the air supply.

The electrodes can be placed at the most suitable distance for the air supply and do not require any adjustment whatever. The control of a large furnace can be effected by a small tumler switch on the high frequency apparatus.

The boiler forming the roof of the furnace cools the fixed gas very effectively because of the latent heat of steam, and at the same time the steam so raised can be used to generate electric energy, so that the combination can work regeneratively.
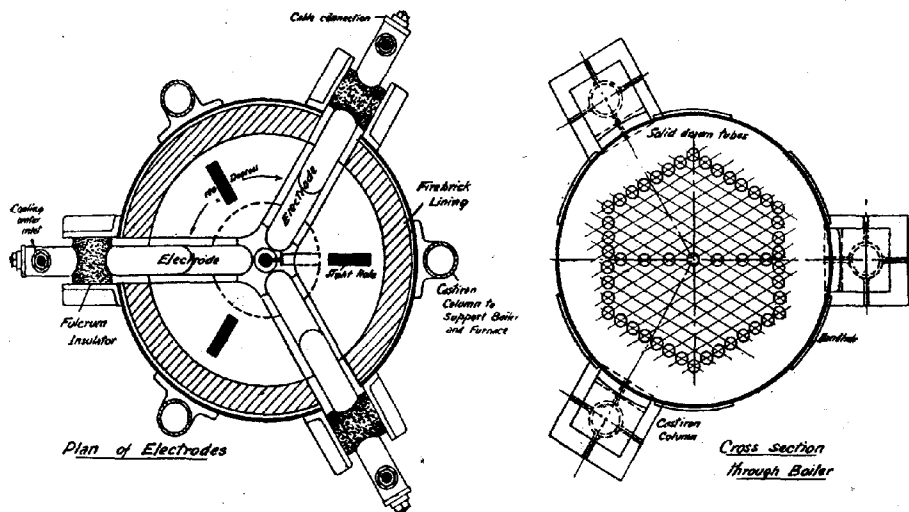

FIG. 8.
Kilburn-Scott three-phase furnace.

The boiler shown has straight tubes, and although it would be better to have a good clean water feed I do not anticipate trouble even if the water should not be very good. Experience with the Bonecourt boiler shows that with very high temperature and good circulation there is little tendency to form scale.

The following may be said to be the special features which distinguish my furnace from those used in Norway and elsewhere.

It is essentially a three-phase furnace using the electric energy exactly as generated, and giving three arc flames within one furnace wall. Also for a given periodicity of supply, thrice as many arcs in a given time as would be the case with single phase.

The three phases give a combined flame of conical shape which is hotter than if the same energy were expended in three separate furnaces because the latter have only a single flat flame and the radiation losses are much greater. The greater bulk of the three phase flame also enables more air to come into contact.

As compared with three single phase furnaces the first cost, the attendance cost, and the maintenance cost are all lower. The space occupied is also much less and there is less brickwork, ironwork, foundations, piping, etc. There are only three electrodes as compared with six for three single phase furnaces and this considerably simplifies the electrical and water connections and the renewing of electrodes, etc.

Method of Working.

The regenerative working is indicated diagrammetrically at the extreme left of Fig. 9. The steam turbo-3-phase alternator may be taken to represent a complete power plant, or it may be merely auxiliary to a bulk supply received from some instance away. A pipe connects the electric furnace boiler to the steam turbine.

The turbine may get its steam from the furnaces only and thus be of a low pressure type, or it may also receive a supply from a main high pressure boiler, in which case it would be of the mixed pressure type. In any case this is well-known steam engineering practice, and so long as steam is available from the furnace boiler good use can be made of it.

Some figures for a furnace plant taking say 1000 kilowatts will show the value of such regenerative working.

One k.w. hour equals 3417 British thermal units of heat, so the plant will absorb 3,417,000 B.Th.U. units per heat.

To evaporate one pound of water into steam at 150 lb. per square inch 1100 B.Th.U. units are required, and assuming an efficiency of only 80% the boiler should give

$$\frac{3,417,000 \times 0.8}{1100} = 2500 \text{ lb. of steam per hour.}$$

A turbo alternator using this steam at the rate of say 16·5 lb. of steam per k.w. hour will thus give

$$\frac{2500}{16·5} = 150 \text{ kilowatts.}$$

That is to say the regenerative value of steam raised by the furnace is about 15 per cent.

The saving may be taken as being fully as much as that because in addition to the saving in electric energy there are a number of incidental advantages in connection with such regenerative working not the least of which is the very effective cooling of the fixed gas.

Of course the steam could be regenerated at low pressure, but that is in no way a disadvantage because low pressure steam turbines' working on a good vacuum are very efficient pieces of apparatus as witness the many exhaust steam turbines now in use. It merely means that more steam would be generated at the lower pressure.

It will be readily seen that the furnaces used in Norway are not suitable for the application of a boiler directly. Utilisation of steam in a prime mover would necessitate generating plant quite different from the water power plant to which they are accustomed and have plenty of. In this country steam generating plant is almost universal, and conditions are in every way favourable to the utilisation of heat; indeed, the ideal combination would be to build a nitric acid factory alongside an existing steam power-station.

Such steam as is raised in the Norwegian plants is merely that necessary for general purposes in the factory for evaporation, etc., and they obtain all they want from the gases after they have been first cooled down to about 100° C. This in itself shows the great amount of heat energy that is wasted.

Three phase current is supplied to the furnace through choking coils and it will be noted in Fig. 9 that near the furnace I have shown diagrammatically an oxygen making plant and a preheater.

The oxygen may come from some process of which it is by-product or it may be made specially, but in any case the question of its purity is quite unimportant. It should be noted that there are two oxygen supply pipes, one joins with the air supply pipe to the preheater and furnace and the other goes to the oxidation tower.

The concentration of nitric oxide has the highest value at each temperature when the product of oxygen and nitrogen is a maximum. It can be shown that it is directly proportional to the square root of the product thus :—Oxygen and nitrogen as in air $=0.21 \times 0.79 = 0.16$. Equal parts oxygen and nitrogen $0.5 \times 0.5 = 0.25$.

Then as

$$\sqrt{\frac{25}{16}} = \frac{5}{4}$$

The increased yield is therefore as 4 is to 5, or 20 per cent.

It is interesting to record that about a dozen years ago Mr. F. Howles, who was then carrying out work in conjunction with the late Mr. Arthur McDougall, published results obtained by enriching the air with oxygen. The production from air was 34 grams of nitric acid per k.w. hour, but double that amount was given by using a mixture of 1 part nitrogen to 2 parts oxygen.

The ideal condition would be obtained by linking up the nitric acid factory with an industrial process which gives off oxygen as a by-product. There are several such industries. For example, the manufacture of hydrogen for aircraft; the manufacture of calcium cyanamide; one method of manufacturing sodium cyanide. There is also the manufacture of hydrogen for increasing the density of oils for margarine, etc.

The production of hydrogen is carried on at the aircraft factory at South Farnborough and some of the oxygen there produced is sent to Woolwich Arsenal and other works for oxy-acetylene welding but this only absorbs a portion of the output.

The oxygen produced in a calcium cyanamide factory is a by-product from the manufacture of nitrogen by the liquid air process, the nitrogen being necessary to convert calcium carbide to cyanamide. At the present time all the oxygen produced at the Odda works in Norway is wasted, because the company is not allowed to bottle and sell it. There are seven Linde plants each producing 350 cubic metres of pure nitrogen per hour, or a total of

2450 cubic metres. The amount of oxygen wasted per hour is therefore $\dfrac{2450 \times 21}{79} = 650$ cubic metres per hour.

This oxygen is pure, because for making cyanamide it is essential to have the nitrogen absolutely pure. Consequently it is very expensive. In the direct furnace process the case is quite different, because the oxygen is only required to raise the percentage of oxygen until it and the nitrogen are about equal. A plant to do this is simple and cheap.

Absorption System.

When the air plus the make-up oxygen passes through the furnace some of it is converted into nitric oxide and we will now trace the progress of the gases as they may be called through the rest of the apparatus.

They first go to a nest of cooling tubes made of aluminium (see top of Fig. 9), over which water is flowing, then through the preheater where some of the heat is imparted to the supply to the furnace, and then to a circular tower made of steel plates lined with acid-proof brick. This is a very large tower, and during the several minutes that it takes in passing through oxidation to nitrogen peroxide proceeds.

It then comes under the influence of the exhauster and passes into the first of the four acid absorption towers (see middle of Fig. 9). Each of these has an acid-proof open-work filling, to allow the gases and the liquor to pass freely through but at the same time bring them into intimate contact.

The gases travel up Tower 1, down Tower 2, up Tower 3, and down Tower 4. Pure water is supplied at top of Tower 4, and passing down forms, with the nitrogen peroxide, nitrous and nitric acids. The nitrous being unstable in an aqueous solution forms into more nitric acid and nitric oxide, and this nitric oxide changes again to nitrogen peroxide, and so on.

The final result is that dilute nitric acid runs out at the bottom, and when it reaches about 5% strength at bottom of Tower 4 it is transferred to the top of Tower 3, where it meets with stronger gas. It is then transferred to top of Tower 2, and so on, on the contra flow principle, gaining strength at each tower until it reaches any desired strength up to about 50%.

After passing the acid absorption towers some gas (up to 20%) still remains, and this can be absorbed either by sodium carbonate or milk of lime to form a solution of nitrate and nitrite, or by caustic soda to form sodium nitrite. Sodium nitrite can be made by fusing metallic lead with sodium nitrate, but the electrical way is much better and cheaper.

In proof of this, it is necessary to refer to the Badische Anilin und Soda Fabrik Works at Christiansand, in Norway, which produces all the sodium nitrite required by the company by electric furnace for direct fixation of nitrogen from air. Previously to the establishment of these works they had supplied all their requirements by the chemical method.

One remarkable feature of the products made by the direct electrical process is their extreme purity. Sodium nitrate made in Norway can compete with the natural Chilian product because of its greater purity.

The movement of the gases through the system is usually effected by fans made of aluminium, and besides those in the pipe line there may be fans to each tower.

Silicon iron or tantiron fans can be used instead of aluminium, and although more expensive in first cost they are a stronger job. Pumps of this metal can also be used for raising the acid from the bottom to the top of the towers.

It may be of interest to mention that the Tantiron Foundry at New Cross has supplied a great deal of acid resisting plant to the electro-chemical factories in Norway. This metal has come to the front very opportunely.

Although it has not been done, the writer sees no reason why the whole operation should not be carried out in a closed cycle. Several chemical operations are carried on in closed cycles, and it is a little curious that this has not hitherto been applied to the nitric acid process.

It will be seen from Fig. 9 that after passing through all the absorption system the gas and air is not allowed to escape into the atmosphere but is brought back to the furnace.

If it were allowed to escape there would of course be great waste of oxygen, but by working in a closed cycle only make-up oxygen is required, and therefore a small oxygen plant will do.

The gain is not merely in the amount of gas fixed, but there is also a considerable advantage in expediting oxidation to nitrogen peroxide.

The several absorption towers, piping, fans, etc., allow leakage, but this will not matter, for the oxygen plant merely keeps the percentage at about 50%, and to provide a little more or less oxygen is immaterial.

Products.

In order to concentrate the dilute acid from the absorption tower it is first heated to drive off some of the water, and this brings it to about 66% strength. Beyond that point more of the water can be removed by sulphuric acid.

This process is purely chemical, and the principles are well known, but of recent years a number of improvements in detail have been made to expedite and cheapen the process. That due to H. Pauling seems to be very effective.

Superheated steam as a heat carrier flows as a counter-current against a stream of nitric acid and sulphuric acid. The steam is gradually absorbed by the sulphuric acid and converted into water, whereby its latent heat is liberated for evaporation of the nitric acid. By using a path of sufficient length, nitric acid of 96% strength is obtained from a mixture containing one part of 48% nitric acid to two parts of 94% sulphuric acid.

Fig. 10 shows a typical lay out of a factory to produce concentrated nitric acid and for the details of concentration plant, and I am indebted to Mr. Glyn W. A. Foster, B.Sc., who was research chemist to H. Pauling's company, the Salterpetrasäure Industrie Gesellschaft, for many years, and who for several months carried out tests on my furnace.

For a good many industrial operations the acid can be used at about 66%, and if manufactured near to where it is to be used, there is no advantage in concentrating from the point of view of cheapening transport. For the manufacture of ammonium nitrate, fertilisers, etc., a strength of 40% or even lower is sufficient.

The manufacture of ammonium nitrate is very simple, as the dilute nitric acid direct from the absorption tower has merely to be treated with ammonia. As we have any amount of ammonia in this country it is obviously an easy and profitable product to make here.

It does not appear to be generally known that the explosives manufacturers in this country for several years have been obtaining supplies of ammonium nitrate from Norway. It has been made at Notodden by merely combining the electrically produced nitric acid with ammonia sent from this country; and as about 75% of the liquor is water, it has meant the carriage of much water and some ammonia to Norway, and finally the carriage of the nitrate back again, a good deal of it going to Nobel's works in Ayrshire.

As may be easily supposed, this business has been very profitable to a few middle-men in this country, whilst money has been going abroad which should have built up a profitable industry here.

It is this kind of thing that has caused scientific and engineering circles in Germany to get the impression of us which they have. One cannot imagine any German shipping thousands of tons of water across the North Sea for the little ammonia it contained, and then buying the product back again at a greatly enhanced price.

Owing to the war the Notodden factory is now about to obtain a supply of ammonia by treating calcium cyanamide with steam.

It was indirectly through this importation of ammonium nitrate that I took up the development of a new furnace. Some years ago I was engaged in lecturing to farmers and others regarding the new fertilisers made by electricity from air. Thinking that the time was ripe for the establishment of a factory in this country, I asked for the terms of a license
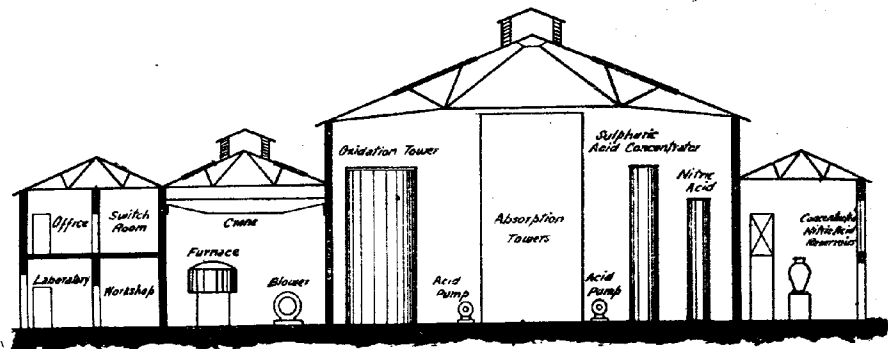
to use the Norwegian furnaces here. It was made very apparent that they did not want the manufacture started here so I decided to develop a furnace.

Later on it may be worth while to make a nitrated phosphatic fertiliser from the waste basic calcareous slag produced by open hearth steel furnaces. The slag from these furnaces is often in an insoluble or tribasic form, and so cannot be advantageously used for agricultural purposes. By treating it with dilute nitric acid or the gases from the electric furnace, a part of the phosphoric acid can be changed into the soluble form, whilst at the same time, lime in the slag is converted into calcium nitrate. The present output by this form of slag in Middlesbrough alone is about 150,000 tons per annum.

a long time. As a matter of fact at the Norwegian factories, the engineers carry on a never-ending series of tests and they are constantly trying modifications.

Samples of the gas are drawn off at regular intervals into large gas bottles which have had the air exhausted from them by a powerful pump. These are temporarily connected with the gas current by opening a tap and a sample of nitric oxide drawn in. This is changed to nitric acid and tested. Then, knowing the percentage contained in the sample, the air flowing through the furnace and the electric energy supplied, the yield can be calculated.

The effect of varying the velocity of the air passing through the furnace is very marked; it is, in fact, one

Elevation

FIG. 10.

Layout of Plant for the direct manufacture of concentrated nitric acid from air by electric power.

Concentration and Yield.

To obtain the best results from a furnace a nice adjustment of conditions is necessary, for there are several factors which influence each other. For example:—

(a) The voltage and current on which depends the heat of the arc flames. (b) The pressure and quantity of air and its velocity through the arc flame. (c) The amount of preheat of the air. (d) The effectiveness of the cooling of the fixed gas. Also a number of smaller factors such as leakage, evenness of air pressure, condition of the electrodes and the furnace lining.

It will be easily seen that with so many variables the adjustment of any furnace for the best conditions takes

of the most important factors in determining on the one hand the percentage concentration of gas and on the other the yield for k.w. hour. A low velocity is favourable to a high percentage concentration, whilst a high velocity is favourable to a high yield per k.w. hour.

At various times extraordinary high percentage concentrations have been claimed. For example: Haber and König state they obtained concentrations of 9·5 to 10% with air at 100 mm. pressure. Brode is also said to have obtained 7·2% with platinum electrodes and 5·8% with iridium electrodes, and he ascribes the lower result to a decomposing influence of the fine particles of the iridium on the nitric oxide in the flame.

On the other hand, Prof. Nernst has given the following percentages as the theoretical maxima for various temperatures :—

Absolute temperature ° C.	Nitric oxide formed %.
1500	0·1
1928	0·5
2202	1·0
2403	1·5
2571	2·0
2854	3·0
3103	4·0
3327	5·0

An interesting point to note about these figures is that as the temperature rises the yield increases at a greater rate. Thus a difference of 369° C. raises the theoretical yield from 1 to 2%, whereas only 224° C. is required to raise the theoretical yield from 4 to 5%.

Since the Notodden factory was first started the percentage concentration of nitric oxide has been doubled, merely by making small modifications in furnace construction and adjusting the air supply and the electric current. Yet the percentage is still under 2%. The fact that it is so much lower than the theoretically possible is really a most promising feature of the direct method, because it indicates the great scope there is for improvement. A process that is highly efficient from the start is a very tame proposition.

High concentration is chiefly beneficial in making the auxiliary plant, absorption towers, etc., more efficient, and as these cost much more than the furnaces it is desirable.

The main thing of course is the yield per k.w. hour or k.w. year. It will be of interest to detail a few of the statements that have been published.

It is convenient to state the yield of a furnace as so many kilogrames of pure nitric acid per k.w. year. It does not mean that pure acid is necessarily made but that the nitric oxide gas coming away from the furnace would if desired produce that amount of pure acid.

Prof. Hofer has calculated the maximum theoretical yield of pure nitric acid per k.w. year as 1850 kgs. with arc flames at 4200° C. and 819 kgs. with arc flames at 3200° C. That is to say, a difference of 225% in the yield for an increase in temperature of only 30%. These are, of course, the yields under laboratory conditions and do not include any auxiliary power, but they serve to show the very great importance of a high temperature.

In actual practice the term electric energy should really include all that is used for working the furnace and not merely the energy of the alternating current arc. For example, it should include the losses in the choking coils and resistances, and in the case of the Birkeland-Eyde furnace the energy taken by the magnetising coils. It should also include the motive power for driving the blowers, etc., because some furnaces require more power to blow the air through them than others. Continuity of working is also most important.

Pauling guarantees 60 grammes of nitric acid per k.w. hour of electric energy measured at the factory switchboard, and this is equal to :—

$$\frac{60 \times 8760}{1000} = 525 \text{ kg. k.w. year,}$$

For 8000 hours a year this gives 480 kg. or just under half a ton per annum.

Dr. Eyde has stated that at the Notodden factory the output per k.w. year is 853 to 938 kgs. of nitrate of lime containing 13% of nitrogen, or reckoned in pure nitric acid, it averages 500 to 550 kgs. with 900 kgs. as the best result.

In another statement the annual production at Notodden is given as 20,000 tons of nitrate of lime, 4000 tons of sodium nitrate and 4000 tons ammonium nitrate. As the Notodden factory is supplied with electric energy from a power house containing four turbo alternators each of 10,000 h.p. or 30,000 k.w. in all, this works out at 0·66 ton of nitrate of lime, 0·133 ton sodium nitrate and 0·133 ton of ammonium nitrate per k.w. year.

The estimate of the annual production of the Saaheim factory has been given as 70,000 tons of nitrate of lime and 8000 tons of sodium nitrite. The Rjukan power house has ten turbine generators aggregating 100,000 k.w.,

so this works out at 0·7 ton of nitrate of lime and 0·08 ton of sodium nitrite per k.w. year.

Averaging up all the above it is safe to assume that a nitrogen fixation plant with single-phase furnaces on existing lines will give the equivalent of half a ton of pure nitric acid 96% per k.w. year, or stated in the other products which are manufactured, say three-quarters of a ton of nitrate of lime, and one-tenth of a ton of sodium nitrate.

Conclusion.

I am convinced that it is possible to considerably increase the present yields, and to summarise briefly the following are some of the reasons :—

Gain by regenerative working.—Theoretically the energy saved by using steam from the boiler to generate electricity is about 15%.

Gain by oxygenated air.—By blowing through the furnace equal parts of oxygen and nitrogen instead of air the yield is increased by 20%.

Gain by increased temperature.—The theoretical yield increases from 819 to 1850 kg. per k.w. year or 225%, when the temperature of the arc flames is increased from 3200° C. to 4200° C. or only 30%.

I claim that a combined three-phase arc flame is hotter and acts on more of the air than three single-phase flames each in separate furnaces, and that, taken in conjunction with the other features of my design detailed above, including the effective cooling, by a boiler, using the steam so raised regeneratively, and also blowing oxygenated air through the furnace, a yield considerably in excess of that obtained in Norway is possible.

When considering manufacture, one naturally thinks first of water power. It is true that such powers as we have are not large ; but the assumption that they are not worth harnessing, or if developed electrical products cannot be made profitable, is quite untrue. The success of the aluminium works in Scotland and North Wales is evidence of that.

As a matter of fact, it should not cost any more, if as much, to harness a water power here as it does to harness a similar one abroad, because the main expense is in the hydraulic and navvying work, the concrete dams, and steel piping, etc. Unfortunately, we are handicapped by difficulties in obtaining necessary authority from Parliament. No doubt in the future nitrates will be made by electric energy from a water power, but it is not necessary to wait for that.

Our main concern is to make nitrates now, and the obvious thing to do is to take the energy of an existing power station, preferably one utilising waste heat. Such stations have a great advantage over water power in being situated in industrial centres where carriage of raw materials and finished products is small.

For solutions such as nitric acid and ammonia the question of carriage is all important, and it is one reason why so many factories have their own plants to make acid from sodium nitrate. The lowest price, however, at which it can be made in that way in normal times is about £18 a ton, reckoned as pure concentrated acid. The electrical method can produce it much cheaper. Working on a restricted hour basis is no disadvantage, because nitrogen fixation furnaces can be switched on and off at any time like arc lamps. They thus make an ideal load for "off-peak" hours.

Although the cost of electricity is higher than in Norway this is not a very material factor, because the carriage of ammonia to Norway and ammonium nitrate back, and especially the carriage of nitric acid over the sea, is several times greater per ton than the cost of power per ton to manufacture the product.

The carriage of such solutions across the sea and on the railway is difficult, for it is not merely a question of finding ships to accept such cargo at reasonable rates, but special heavy tanks have to be provided and to be maintained. As a matter of fact, the carriage of nitric acid from Norway has not been attempted.

Even if Norway could compete, the establishment of factories in this country to make nitric acid, ammonium

nitrate, and sodium nitrite from the air is a national duty. They are urgently wanted for explosives and for the aniline dye industry.

Now that a Special Committee has been appointed to assist in the establishment of chemical industries hitherto carried on abroad, I hope it will not be long before we have factories for producing nitrates from the air by electric power.

DISCUSSION.

The author was asked what would be the smallest practicable commercial unit. One of the main advantages of Pauling's furnace was, that it could make small quantities of acid, such as were used in many manufacturing processes, and at a reasonable cost.

Mr. KILBURN SCOTT said he would naturally prefer to work continuously and on a large scale, but the direct electric process could be economically worked on a moderate scale and also intermittently. His idea of a small commercial unit would be about 1000 kilowatts, having say three furnaces of 330 kilowatts each. A thousand-kilowatt plant, including furnaces, absorption towers, circulating fans, piping, and all auxiliary apparatus, but not including the steam turbine which he proposed should be a part of the system when working regeneratively, could be put down for something like £6 or £7 a kilowatt. Of course, the larger the plant the lower the cost per kilowatt: thus for a 10,000-kilowatt plant the price per kilowatt would come down to £5 or £6 per kilowatt. This price per kilowatt was a convenient way to state the cost of the installation, but it must be understood that the bulk of the £5 or £6 was not for furnaces and electrical gear but for the absorption towers, circulating fans, piping, and other non-electrical apparatus. The purely chemical part of the plant was the most expensive and occupied most space. It would be feasible to start with a smaller plant than one of 1,000 kilowatts; for example, one might have first a 330-kilowatt furnace, then add another 330, and so on, or the units might be two of 500 kilowatts each. He did not think it would be commercially advisable to go smaller, but it all depended on local conditions and the cost of energy and of carriage.

Mr. G. NEVILL HUNTLY said that some seven or eight years ago he tested a nitric acid plant by Moscicki. The main point claimed by the inventor was not that the yield of nitric acid per kilowatt-year was notably increased, but that the concentration of nitric oxide was greater. He thought that at that time the concentration at the Notodden works in Norway was about 0·75%. The Moscicki furnace was said to give about 2%, and the inventor claimed for that a considerable saving in the capital cost of the absorbing system. As the Moscicki furnace had not been mentioned by Mr. Kilburn Scott, he assumed it had not been commercially successful, although the inventor was one of the pioneers in the preparation of nitrates from the air.

Mr. KILBURN SCOTT said that all the furnaces in use abroad worked with a single-phase arc, and whether the arc flame was produced one way or the other, as a long-standing arc blown by a whirling current of air, or magnetically directed as in the Birkeland-Eyde and Moscicki furnaces, the temperature and electrical conditions were pretty much the same. Also, as the cooling was effected by excess air in all these single-phase furnaces the possible concentrations would not vary much; they all appeared to give 1½ to 2%, depending on the velocity of the air. All single-phase furnaces at present in use had certain inherent defects, and the concentration and yield was limited thereby. His own furnace had a 3-phase arc flame which was hotter and of better

shape to ensure contact with the air than single-phase flames, each in a separate furnace. The radiation losses of the 3-phase furnace were much lower, and it had many other advantages which he had pointed out. The hotter flame gave better results, and the efficient cooling by the boiler also gave more fixed gas, whilst at the same time generation of power by steam from the boiler would materially reduce the total power drawn from the main supply. These improved conditions would give both a higher concentration and a higher yield, but of the two he considered the yield was the most important.

The author was asked if the presence of moisture in the air and the introduction of steam influenced the equilibrium. Also, did air pressure influence the yield?

Mr. KILBURN SCOTT said that Professor Guye had stated the yield was increased somewhat if the air was freed from moisture. If there should be a water leak from the electrodes the yield would drop immediately. As to the use of high pressure opinions differed widely. In 1907 Briner and Durand obtained higher percentages by lowering the pressure. Schönherr claimed that the vertical movement of the ascending current of air lowered the pressure in the centre of the air column, and that tended towards higher yields. On the other hand, Muthmann and Hofer in 1903 noted that while using the higher temperatures of the electric arc a marked increase in yield accompanied the use of compressed air. Rossi, in some experiments with air up to 50 atmospheres, is said to have succeeded in converting one-third of the oxygen present into nitric oxide and securing concentrations of 16% NO. Haber experimented in 1910 with a small Schönherr furnace with pressures up to 20 atmos., and was led to the conclusion that an increase of pressure offered no practical advantage. Personally he (the author) thought there would be a number of mechanical difficulties in getting high pressures inside commercial furnaces constructed of refractory bricks for all such linings were porous. In the construction of electric furnaces a number of electrical details had to be carefully considered. For instance, when dealing with alternating electric currents inside a steel structure, it was necessary to avoid " eddy currents," i.e., currents induced in the steel structure. The efficient insulation of the electrodes where they passed through the wall of the furnace was also important. Great pressures could be attained in laboratory apparatus which were quite out of the question on a commercial scale. No doubt an electric furnace for fixation of nitrogen could be made tight against high pressures, but it was not clear that there would be sufficient advantage to make it worth while. The direct process gave good results without high pressure. Regarding depreciation he did not think it would be more than 10%. The lining of his furnace was remote from the arc flames, being behind the electrodes, and it was a very simple firebrick structure. The depreciation of the boiler would be higher than that of the furnace proper, but on the other hand depreciation on the absorption towers was very low. They were built on the lines of a brick chimney, and it was usual to allow only 2% for depreciation there. As the absorption plant formed the largest and most expensive part of the plant, 10% depreciation on the cost of the whole system was ample. There was no expensive catalyst or other expensive material to renew. There was nothing to go wrong with the furnace; it was more robust than an arc or induction furnace for smelting metals. He agreed with Mr. Lymn that by-product recovery was the proper way to generate power from coal, and that if produced in that way it could be sold in bulk for a 24-hour supply at a price that would compare

favourably with Norwegian water power. It would of course be more profitable to run the plant 8760 hours per year, as against the restricted hour basis of 5200 hours a year. At the same time these furnaces could be switched on and off at any time. Under such conditions a certain amount of heat energy would be lost by radiation during the periods of stopping and starting. That might be got over by passing a certain amount of current through a heating rheostat at a low voltage so as to keep the lining, etc., warm during the standing hours.

Mr. A. H. LYMN said that the capital cost of nitric acid plant in Norway had been very high indeed. It would be interesting to know what was Mr. Kilburn Scott's idea as to cost of a plant for direct fixation of nitrogen. The author had omitted to mention the production of power by making producer gas and simultaneously recovering by-products. If such a plant were erected near collieries where suitable coal was obtainable, the gas could be obtained for nothing, or even at a profit. By utilising this gas either in large gas engines or under steam boilers and utilising steam turbines, power costs of 0·1 penny per kilowatt-hour could be attained in Great Britain, not on the restricted service basis of 5200 hours a year, but continuously for 8760 hours per annum. He (the speaker) had installed such plants for the Badische Anilin und Soda Fabrik, and also for the Hoechst Farbwerke, for electro-chemical purposes, to use even comparatively expensive coal. It was probable that the electric furnace could be utilised much more profitably if it could be worked continuously.

Mr. W. F. REID said that perhaps Mr. Kilburn Scott had not had the opportunity of trying his boiler on a large scale ; others had found it was not practicable to expose a boiler to such a great heat. The heating of the water might possibly be managed, but the nitrous gases corroded the metal very rapidly. The great difficulty was to cool the gases as soon as possible after the initial fixation of the nitrogen, because otherwise the nitrogen compounds produced were decomposed again by the heat. In the Pauling process the gases were cooled in a very ingenious way by means of an English invention. The stoves designed by Cowper to heat the air supply for blast furnaces were used, but the process was reversed. There were two of them in the plant shown in one of the figures. The hot gases and air passed through the chilled brickwork, and the brickwork took up the surplus heat. The two chambers were used alternately, so that the gases could be chilled without great wear and tear. He had not the slightest doubt, in view of the experience already gained on the matter, that 10 % depreciation of a boiler in that position would not be nearly enough. The absorption of the gas seemed to him to be a great problem. A small quantity of a valuable product had to be absorbed when mixed with a very large quantity of gas. He had visited several of the factories, and at most of them large volumes of orange fumes were escaping at the exit. The bulk of the nitric acid used in this country must be concentrated ; dilute acid was of very little use. In some of the factories an ordinary tower was used like those used to concentrate waste acid in explosives factories, which worked fairly satisfactorily. He was inclined to think that the future of the industry would lie in the oxidation of ammonia made from the atmosphere. Large quantities of nitric acid were being made in Belgium by that process, until the Germans interrupted it. There was no necessity to take the ammonia from this country to Norway in order to get nitrate of ammonia when they had the means of producing it from the atmosphere. In the direct electric process a small quantity only of the electric power was utilised in producing combination of the two gases. If the waste heat could be

economised, and power produced in some better way than Mr. Kilburn Scott suggested doing with his boiler, a great proportion of the power might be economised. So far he was not aware of any process that did that, but it would give enormous economy. It would be a more efficient process if the only energy lost was that employed in the actual combination. Mr. Kilburn Scott placed the minimum power required for a factory very low indeed when he said 1000 H.P. If anybody had surplus power they might utilise a portion to make nitric acid. Personally, he would not advise the erection of plant under 40,000 or 50,000 H.P. He quite agreed with what had been said with regard to producer gas power. With the utilisation of waste products on the spot where the stuff was wanted and used, he thought they could compete with a factory which had in the first instance to put up plant to utilise water power. The cost of harnessing water power was very considerable, and they usually had to carry the material a very great distance, and the carriage of such materials at the present time was a serious matter. He had sought out all the water power in Scotland, but the biggest sources were taken up, and the reason the others were not utilised was because it would not pay on such a small scale.

Mr. KILBURN SCOTT said that it was not until the nitric oxide changed to nitrogen peroxide that it attacked metal, and that change did not take place until the temperature had dropped to below 600° C. Now the temperature of the arcs in these furnaces was somewhere about 3000° C., whilst the temperature at which the gases left the furnace was just under 1000° C. For example, Eyde had stated that the gases left his furnace at between 800° and 1000° C., and Schönherr had given about the same figures. Now 900° C. was below the temperature at which gases entered the tubes of high-class boilers. Boilers were used in Norway for the purpose of raising steam for various industrial purposes in the factory ; in fact, evaporation of the products was about the only purpose they had to use the steam for. The gas entered the boilers at about 400° C., and left at about 200° C. Therefore it was clear that the gas went into the boilers at under the temperature at which it had changed into nitrogen peroxide, and as already stated it was not until it had changed into nitrogen peroxide that it attacked metal. He thought 10 % depreciation was enough.

The Cowper stoves installed at the plant in the Haute Alpes were at some distance from the furnaces, and their purpose was solely to cool the gases and not to prevent dissociation. Dissociation must be prevented in the furnace itself, and in the Pauling furnace it was effected by blowing a separate supply of cooling air into the top of the arc flames. Before the gases reached the Cowper stoves they had already passed through the preheater. The most scientific and efficient way to cool the fixed gases was to take advantage of the latent heat of steam to absorb the heat rapidly. With regard to acid concentration, it was well known that acid could be brought up to 66 % by mere heat evaporation. The absorption towers would give up to 50 %, but up to 30 or 40 % strength would do to make such products as calcium nitrate and ammonium nitrate. The Ostwald catalytic process in use in Belgium, at Vilvorde, made the acid at 40 to 50%, so that for the higher concentrations the sulphuric acid plant was required for that just as for any other process. As regards the minimum horse-power advisable for the plant, one nitric acid factory complete with Cowper stoves worked by power from a glacial stream, etc., absorbed only 4000 kw., having nine furnaces of 450 kw. each. Another plant which had been running most successfully in Italy for many years with energy purchased from a power company took 7500 kw. Ten years

ago the largest plant in Norway was of only 120 kw., capacity. A nitric acid factory at Legnano, near Milan, which had been using Pauling furnaces for many years worked on that restricted service. It used 7500 kilowatts, and electric energy was supplied by a power company during the off-peak hours at 20s. per kilowatt-year.

One considerable source of waste power which could be readily harnessed for the electric production of nitric acid was that of modern by-product coke oven plants, which gave a surplus of about 50 % of the whole gas produced. Mr. Twynam, of Middlesboro, and himself were interested in a proposal to convert this waste gas into electrical energy, then utilise the energy in a Kilburn-Scott furnace for the production of nitric acid, and finally combine the nitric acid with the ammonia in the whole of the coke oven gases so as to form nitrate of ammonia. Figures which had been got out showed that it would be more profitable to use the surplus gas and the ammonia in that way than merely to make the less valuable sulphate of ammonia, as at present, the sulphuric acid for which had to be purchased.

The Ostwald patents for making nitric acid by the catalytic process taken out about a dozen years ago, were transferred in April, 1910, to a company called Nitrates, Ltd., promoted by Mr. A. S. Barton. Not only had there been no profits, but Mr. Barton had admitted that the process had been most inefficient, and £78,604 had been spent in twelve months on account of the factory.

Meeting held at Burlington House on Monday, February 1st, 1915.

MR. W. F. REID IN THE CHAIR.

Specimens of chemicals and apparatus were displayed, which hitherto have been mainly produced abroad, but now are being manufactured in this country.

The following is a list of the exhibitors and products :—

Messrs. Baird and Tatlock, Ltd. (London).— Glass apparatus of their own manufacture, porcelain boats and crucibles, thermometers, burettes, and reagent chemicals.

Messrs. W. and R. Dalston, Ltd. (Maidstone).— High-grade filter papers, suitable for laboratory analysis.

Messrs. A. Boake, Roberts and Co., Ltd. (Stratford).—Anethol, eugenol, citral, citronellal, geraniol, triacetin, terpeneless oils of lemon and ginger.

The British Glass Wool Co. (2, Compton Road, N.).—Glass wool.

The British Laboratory Ware Association, Ltd.— English-made glass beakers, flasks, tubing, etc., Doulton porcelain ware, and Royal Worcester porcelain crucibles, etc.

Messrs. Butterworth Bros., Ltd. (Newton Heath, Manchester).—Glass tubing, Tenax leadless resistance glass, canes for tungsten wire.

Corticine Floor Covering Co., Ltd. (Aldersgate Street, E.C.).—Articles of compressed cork.

Messrs. Higgins Bros. (Liverpool).—Salicylic acid.

Messrs. Johnson and Matthey (Hatton Garden, E.C.).—Magnesium metal and powder, barium platinocyanide for X-ray screens.

Manchester Oxide Co. (Manchester).—Pure barium and ammonium sulphocyanides.

Morgan Crucible Co., Ltd. (Battersea, S.W.).— Combustion and pyrometer tubes.

Messrs. James Powell and Sons (Whitefriars Glass Works, E.C.).—Glass flasks and tubing.

Messrs. A. G. Thornton, Ltd. (Manchester).— Sectional papers, true to scale, replacing German-made products.

After a brief description of the exhibits had been given, Mr. J. J. EASTICK moved a resolution urging the Government to take such steps as would tend to the production and refining within the Empire of sugar sufficient for the Empire's consumption. The resolution was supported by Capt. G. L. Courthope, M.P., Mr. C. S. Parker, Mr. W. T. Chadwin, and Mr. Buckmaster. Further discussion was adjourned till March 1st, 1915.
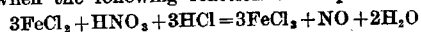

Manchester Section.

Meeting held at the Grand Hotel, on Friday, December 4th, 1914.

MR. JULIUS HÜBNER IN THE CHAIR.

A RAPID METHOD OF ESTIMATING NITRATES.

BY EDMUND KNECHT.

The oldest method for the quantitative determination of combined nitric acid is that of Pelouze, in which a known weight of the substance to be assayed is boiled with excess of ferrous chloride (or sulphate) and concentrated hydrochloric acid when the following reaction takes place :—

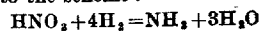$$3FeCl_2 + HNO_3 + 3HCl = 3FeCl_3 + NO + 2H_2O$$

The remaining ferrous chloride is then estimated either with standard bichromate or permanganate. An alternative method (Knecht and Hibbert, " New reduction methods in volumetric analysis," p. 67) is to estimate the ferric chloride directly by means of titanous chloride.

The nitrometer of Lunge affords a rapid and accurate means of estimating combined nitric acid, and is perhaps the most universally used, especially in works practice. It is based upon the fact that nitrates, in presence of concentrated sulphuric acid and metallic mercury, yield the whole of their nitrogen as nitric oxide, which is measured directly as such.

A third method is a gravimetric one and is based upon the property of diphenyl-endanilohydrotriazole (Nitron) of forming a sparingly soluble precipitate with nitrates.
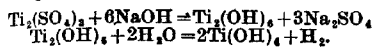
A fourth method of estimating nitrates is based upon the quantitative reduction of nitric acid to ammonia in presence of excess of caustic alkali by means of a suitable reducing agent, according to the scheme :—

$$HNO_3 + 4H_2 = NH_3 + 3H_2O$$

The ammonia formed is collected in standard sulphuric acid and the extent of the neutralisation of this is ascertained by titration with standard alkali, or in case very small quantities only are present the distillate is nesslerised. The reducing agent originally employed in this method was zinc dust, but later it was found that aluminium was more suitable for the purpose. In both cases, however, a considerable amount of time was considered necessary to effect complete reduction.

In a paper published in 1903 (Ber., 36, 166; this J., 1903, 232) the author drew attention to the fact that titanous hydroxide was capable of effecting the complete reduction of nitrates to ammonia. A further examination of this reaction showed that the reduction is almost instantaneous.

When caustic soda is added to a solution of a titanous salt, black titanous hydroxide is precipitated, but this begins to decompose almost at once, yielding nascent hydrogen and the white titanic hydroxide, probably according to the following equations :—

$$Ti_2(SO_4)_3 + 6NaOH \rightleftharpoons Ti_2(OH)_6 + 3Na_2SO_4$$
$$Ti_2(OH)_6 + 2H_2O = 2Ti(OH)_4 + H_2.$$

The new method, or rather the modification of the old method, is based upon this reaction, and when properly carried out has given entirely satisfactory results.

A convenient amount of nitrate for a single estimation is about the equivalent of 0·1 grm. potassium nitrate. Thus, in the assay of a commercial sodium nitrate, about 1 grm. is accurately weighed, dissolved in water, and made up to 100 c.c. Of this, 10 c.c. are measured into a copper flask, excess of caustic soda is added, and then about 20 c.c. of commercial titanous sulphate or chloride. The distillation can then at once be proceeded with and, after the boiling has been continued for a quarter of an hour, the operation is finished and back titration is effected.

It is essential that the reagents should be added in the sequence as stated, for if the acid solution of the titanous salt is allowed to react with the nitrate, reactions take place which result in the expulsion of a portion of the nitrogen either as nitrous or nitric oxide, and the result is consequently unreliable. It is also obvious that the titanous salt should be free from ammonia. Personally I have not had any trouble in this respect, but I am informed that ammonia has been found in small quantities in some of the older commercial products. In the newer products, however, this is not the case, and the price need not be a deterrent, for two estimations can be carried out at a cost of the reagent of considerably less than one penny.

Two estimations carried out in the manner described on pure potassium nitrate gave respectively 99·80% and 99·83%. The results have been corroborated by different observers and have invariably revealed the reliability of the process.

Nitrites are also quantitatively reduced to ammonia by the action of titanous hydroxide in presence of excess of caustic alkali. This was shown to be the case by a duplicate experiment with pure crystallised silver nitrite, which yielded in both cases 99·47% AgNO₂.

The quantitative reduction of nitric acid to ammonia by the lower oxide of a metal as described in the above short note is, I believe, the only instance of its kind, and I am convinced that the method affords the most rapid of all existing processes for the exact estimation of combined nitric acid. Any curtailment of time required for such an estimation is a gain to the analytical chemist and indirectly to the industries. The method has been introduced with success into the practical curriculum of the Chemical Department of the Municipal School of Technology, Manchester.

DISCUSSION.

Dr. T. J. I. CRAIG said that all the titanous sulphate made in the Manchester Alum Works was now free from ammonia. Aluminium amalgamated with mercury reduced nitrates in acid solution, and it was employed in one laboratory in the Manchester for sewage and water analysis ; when small quantities of nitrate were present a piece of aluminium was amalgamated by immersion in a dilute Nessler solution. The sample of water was poured on, and acid was added, and in two hours the nitrates were reduced to ammonia

which was then distilled off and determined. He had tried Prof. Knecht's new process and found it reliable.

Mr. J. H. LESTER pointed out that the use of aluminium amalgam was adopted by himself in 1888, at the suggestion of Dr. Ormandy.

Professor KNECHT, in reply, said that he had not tried aluminium amalgam, but could quite understand that it would work more rapidly than aluminium alone. Copper vessels were used because they prevented the " bumping " which occurred rather badly in glass, and also after the titanous hydroxide had been precipitated, it was difficult to clean the vessels, as it adhered very firmly to the glass. He could not say definitely whether very dilute solutions of nitrates would be instantaneously reduced,' but the reason why the titanous hydroxide acted so rapidly was that there was a very large surface, probably something like a thousand times as great as with a metal, and consequently the reduction was very much more rapid. He should imagine that in very dilute solutions nitrates would be instantaneously reduced. He could not say whether organic matter would disturb the course of reaction.

Nottingham Section.

Meeting held at Nottingham, on Wednesday, December 9th, 1914.

MR. L. ARCHBUTT IN THE CHAIR.

DISCUSSION ON A " RAPID AND ACCURATE METHOD FOR THE DETERMINATION OF CARBON IN IRON AND ITS ALLOYS."

BY DR. ERNST SZÁSZ (this Journal, 1914, 994).

Mr. T. H. ADAMS said that the rapidity of the method was for some classes of work very desirable, provided that accuracy could be obtained, but this he rather doubted. He strongly deprecated the patenting of an analytical method as tending to hinder research. The amount of steel burnt was small compared with the amount usually taken for the direct combustion process. The preliminary purifying train for the oxygen was, in his opinion, unnecessarily complicated. He could not see the necessity for the incandescent platinised asbestos, as compressed oxygen prepared, as was the greater proportion made in this country, from liquid air could hardly contain any tangible quantity of carbon monoxide or hydrocarbons. In his opinion the best method was first to burn steel of well-verified carbon content each day before commencing any unknown samples. If the correct result was obtained it was proof that all was in order. When working in this way the only preliminary purifying train required was a soda-lime tube and a valve flask of sulphuric acid similar to the one described in the paper. The oxygen gas holder was also unnecessary. For years he had worked from a cylinder with an ordinary reducing valve with satisfactory results. It seemed probable that the capacity of the combustion tube together with the connecting tubes and condenser was at least 60—70 c.c. The total capacity of the measuring vessel was only 150 c.c., and this was not completely filled by the evolved carbon dioxide and the oxygen used for washing out. It seemed, therefore, that all the

carbon dioxide had to be washed out by about an equal volume of oxygen, that is, the apparatus was only once rinsed out by oxygen: that was not enough. If the process had been given about double the time and used as a gravimetric process it would have been better. The necessary temperature in the furnace to induce the commencement of the rapid absorption of oxygen by the steel was, in his experience, about 1000° C., and the figure given by the author, 1150° C., was really higher than was necessary, but perhaps that was a vital point in the process when extreme rapidity was required.

Mr. BERNARD COLLITT said that the estimation of carbon in steel by direct combustion in a current of oxygen was thoroughly worked out in England before adoption in America and Germany, and was described by Dr. John E. Stead at the 1904 meeting of the Iron and Steel Institute in America; he stated that his attention had been drawn to the method by one of his old pupils who had used it successfully as early as 1890. The use of a preheating tube or furnace to burn organic matter in the oxygen to carbon dioxide was recommended in the standard method of the American Foundrymen's Association six years ago or more. He failed to see the necessity of drying the oxygen before it reached the steel. Over 30 years ago Prof. J. O. Arnold had shown that chemically dry oxygen would not unite with bright steel turnings at a full red heat; Hilpert (Ber., 1913, 46 ; this J., 1913, 509) stated that whilst with dry oxygen a temperature of 1200° C. was necessary for the complete combustion of steel and iron, with moist oxygen a temperature of 950° C. was sufficient. Besides eliminating the calcium chloride tube for the oxygen entering the combustion tube, could not the chromic acid bulb for the leaving oxygen be also eliminated by using as sealing liquid for the gas a solution of sulphuric acid (1 to 10) containing some dissolved chromic acid ? The measurement, instead of weighing, of the carbon dioxide produced by the combustion of carbon in steel, etc., had been suggested by Wiborg in 1887. It was impossible to find any difference between his method and that described by Wirtz in "Stahl und Eisen " in 1913, where it was claimed that carbon estimations in steel " analytically exact and faultless " could be made in three to four minutes at a cost of 1½d. per estimation. The apparatus was different, but the methods were identical.

The CHAIRMAN said he had experimented with the direct combustion process ten years ago, when Dr. Stead described in the Journal of the Iron and Steel Institute his method in which the steel drillings were mixed with manganese ore. It was soon found to be unnecessary to mix anything with most steels, and that the sole condition for success was to get the right temperature, which must be in the neighbourhood of 1000° C. The steel, while burning, absorbed the oxygen as fast as it could conveniently be passed in, and the form of combustion apparatus used was governed by the method of measuring the CO_2 formed. The very ingenious apparatus described by Dr. Szász, no doubt, answered admirably the inventor's purpose, and gave correct results. But it would be absurd to put up an expensive and complicated apparatus of that kind unless a very large number of analyses had to be made regularly in a very short space of time. In an ordinary laboratory, dealing with only a few samples of steel per day the analyst would find it more economical and convenient to use the much simpler apparatus necessary for absorbing the CO_2 and weighing it. A moderate number of samples daily could be dealt with in that way without the constant attention needed by Dr. Szász's apparatus, and time left for other work to be carried on by the same operator. The oxygen usually supplied in cylin-

ders in this country needed no such elaborate purification as Dr. Szász described, but it was desirable to pass it through a simple purifying train containing soda-lime, calcium chloride, and a sulphuric acid drying tube. If it was necessary to work much more rapidly, the CO_2 might be measured by means other than weighing. There were several ways in which it could be done, and Dr. Szász's method was one of these. He did not think there was anything in his particular method which radically modified what they already knew.

Obituary.

CARL LIEBERMANN.

Geh. Rat. Prof. Dr. Carl Liebermann died in Berlin on Dec. 28th, 1914, at the age of 73. In his early years he was assistant to Prof. Adolf Bayer, and in 1879 was appointed Professor of Organic Chemistry at Charlottenburg, a post which he held until his death. He will always be remembered for his work in connection with the synthesis of alizarin. Having recognised that natural alizarin was a derivative of anthracene, Graebe and Liebermann in 1869 succeeded in preparing alizarin by fusing dibromoanthraquinone with caustic potash, and in the same year, Graebe, Liebermann, and Caro discovered that anthraquinonesulphonic acid was converted into alizarin by fusion with caustic potash (see W. H. Perkin; this J., 1885, **4**, 432). Liebermann made an extensive investigation of other dyestuffs, including aurin, pittacal, brazilein, quercetin, xanthorhamnin (rhamnetin) archil, cochineal, and catechu. He also carried out much valuable research in connection with the alkaloids, particularly those of coca, and his method for converting ecgonine into cocaine is used at the present time. He was successful in synthesising isonarcotine, cinnamylcocaine, and the two truxillines, in isolating hygrine and cuscohygrine from cusco leaves, and in elucidating the constitution of tropacocaine, opianic acid, and the truxillic acids.

MAURICE BRICKDALE LLOYD.

Captain M. B. Lloyd, late of the Royal Artillery, was born in 1865, received his first commission in 1884, and served for some years in India as lieutenant and captain in the R.H.A. Later he passed into Woolwich, and at the conclusion of the two-year course was appointed to the staff of the College as Instructor in Chemistry and Electricity, which appointments he held until transferred to the Home Office as an Inspector of Explosives. As an Inspector he did valuable work for the Government, and conducted inquiries in several cases of public interest. Leaving the Army, he became, in 1908, a director of Curtis's and Harvey, Ltd., where his technical knowledge, particularly in the location and construction of danger buildings and as to naval and military ammunition, found ample scope. He was a member of the War Office Committee on Shipments of Explosives and of the Celluloid and Abel Heat Test Committees. He also compiled a booklet on the construction of stores and magazines for explosives, and the Home Office regulations concerning them.

He died, after a short illness, on February 5th.

Journal and Patent Literature.

I.—GENERAL PLANT; MACHINERY.

PATENTS.

Cooling air to low temperatures ; Process of, and apparatus for ——, *also applicable to the production of ice.* R. P. van Calcar, Begstgeest, J. Ellerman and J. H. Martijn, The Hague, Holland. Eng. Pat. 2950, Feb. 4, 1914. Under Int. Conv. Feb. 26, 1913.

A CURRENT of air is drawn by a fan through a closed chamber into which a volatile liquid, such as ether, ethyl chloride, or the like, is also introduced. The cooling produced by the evaporation of the volatile liquid condenses the moisture as frost or snow, which is deposited on the surface of a layer of sodium or calcium chloride or other salt capable of forming a freezing mixture with snow or ice. The basket or cage containing the salts surrounds a vessel containing water, which is frozen by the cold produced. The cooled air, after leaving the chamber, is passed through another chamber cooled externally and having a number of globular expansions which form baffles and impart a whirling motion to the air. This causes the condensation and deposition of the volatile liquid, which is collected for re-use.—W. H. C.

Gases ; Apparatus for washing ——. W. B. Davidson, Birmingham, and A. J. Liversedge, Croydon. Eng. Pat. 19,028, Aug. 25, 1914.

THE patent relates to apparatus in which the gas enters the compartments of the washer at the bottom near the side and meets a spray of washing liquid produced by a centrifugal device mounted on a central vertical shaft. To prevent the spray from entering the gas-inlet passage, a grid composed of substantially vertical, concentric, annular plates, or of one or more strips wound spirally, is provided, in conjunction with a curved deflector over the gas passage. The washing effect is increased by the thin streams of liquid flowing down the plates of the grid. The device may be applied not only to gas-washers of the type described in Eng. Pat. 9302 of 1914 (see this J., 1914, 1082 ; in the figure there given, 3 is the grid and 2 the deflector), but also to other washers, such as the Feld sprayer.—A. S.

Gases of low boiling point ; Apparatus for cooling and liquefying ——. Industriegas-Ges. für Sauerstoff- und Stickstoff-Anlagen m. b. H. Ger. Pat. 276,977, April 18, 1912. Addition to Ger. Pat. 198,503.

IN the apparatus described in the chief patent (see Fr. Pat. 446,560 ; this J., 1913, 142), the cooling tube is enlarged, or a vessel is interposed, at a place where the temperature is below the liquefying point of the more easily condensable gas. Any liquefied or solidified material which passes from the receiver proper into the cooling tube, is retained in this enlargement or vessel, and the less easily condensed constituent passes on to the final portion of the cooling tube, where it is cooled to its liquefying point.—A. S.

Transmission or exchange of heat between fluids ; Apparatus for the ——. A. D. Harrison, Wolverhampton. Eng. Pat. 4252, Feb. 18, 1914.
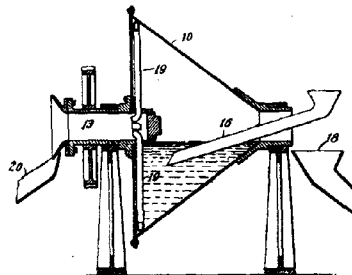
To allow for the alteration in volume of the fluids flowing in opposite directions through a heat-inter-

changer, the latter is built up of plates bolted together and having two non-communicating, adjacent passages or series of passages between them, the flanges and baffles which constitute the walls of the passages being so arranged that the cross-section of the passage for the fluid being heated increases and that for the fluid being cooled decreases from the inlet to the outlet.
　　　　　　　　　　　　　—W. H. C.

Separating coarse particles from divided material. H. W. Hardinge, New York, U.S.A. Eng. Pat. 11,213, May 6, 1914.
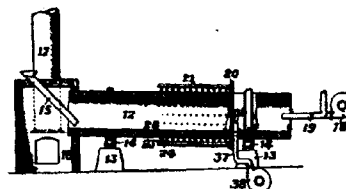
THE material is mixed with water and fed through the shoot, 16, into the rotating conical barrel, 10. The coarse particles settle to the lowest part of the

barrel and are scooped up by the conveyor pipes, 19, and discharged through the hollow shaft, 13, into the shoot, 20. The finer material is discharged from the smaller end of the barrel into the shoot, 18.—W. H. C.

Furnace or kiln ; Rotary ——. G. F. Downs, Buffalo, N.Y. U.S. Pat. 1,121,906, Dec. 22, 1914. Date of appl., April 25, 1914.

A CIRCULAR head, open at one end, is mounted upon a rotary cylindrical furnace (see figure), and is connected by manifolds and pipes with the

interior of the cylinder, and by its open end, during part of the rotation, with a wind-box to which gas or air under pressure is supplied. When not in communication with the wind-box, the open end of the manifold is closed by a plate held against it by a spring.—W. H. C.

Distillate condenser and steam generator. C. L. Suhr, Oil City, Pa. U.S. Pat. 1,122,169, Dec. 22, 1914. Date of appl., April 7, 1914.

THE vapours from the still are led downwards and around the tubes of a horizontal tubular heater, to

a coil condenser. Water is passed through the heater, and the steam given off is passed into the still. The supply of water and the discharge of steam are controlled by float-valves.—W. H. C.

Filtering colloidal materials; Apparatus for ——. J. von Kruszewski. Ger. Pat. 275,888, Dec. 23, 1913.

THE material is passed successively through two or more sieves, arranged in series. The sieves, or one or more of them, are coated with fat or the like, or treated in any other way to render them incapable of being wetted by the liquid passing through. With this arrangement considerable quantities of colloidal slime can be filtered clear, in a short time, without the use of high pressure.
—A. S.

Treating liquids or solids with gases, liquids or mixtures of these; Apparatus for ——. R. Timm. Ger. Pat. 276,119, Oct. 5, 1913.

A RECEPTACLE for the material under treatment rotates about a horizontal or inclined axis, on hollow bearings, the median axis of the receptacle

intersecting the axis of rotation, between the bearings, at such an angle that the centre of gravity of the empty receptacle lies on the axis of rotation. Several such receptacles, communicating one with another, may be mounted, in series, about a common axis, as shown in the figure ; the arrangement may be such that the centres of gravity of the receptacles next to the bearings, *b*, lie outside the axis of rotation, CD, but the centre of gravity of the complete series of receptacles lies on the axis. The receptacles may be fitted with perforated partitions, *i*, the perforations in adjacent partitions being so arranged that a certain number of them are always covered by the liquid or solid under treatment. The apparatus is especially suitable for dissolving solids and preparing suspensions.
—A. S.

IIA.—FUEL; GAS; MINERAL OILS AND WAXES.

Coal and coke; Determination of ash in ——. F. Weisser. Chem.-Zeit., 1914, **38**, 1264—1265, 1289—1290.

THE ash-content of coal determined by incineration is always lower than the true content of mineral matter, chiefly owing to the conversion of carbonates into oxides during ignition, and the results obtained over a naked flame in an open dish are higher and more accurate than those obtained in a muffle, because in the former case the loss mentioned is partly compensated by fixation of sulphur dioxide from the gases of the flame (see this J., 1912, 674). In coke, however, the quantity of carbonates present is almost negligible, and the ash-content determined by incineration tends to be high, owing mainly to the oxidation of the sulphur to sulphates and, when a naked flame is used for heating, to the absorption of sulphur dioxide. If the weight of ash obtained, whether over a naked flame or in a muffle, be diminished by subtracting the weight of sulphuric anhydride present in it, the result accords closely with the true content of mineral matter in the coke. By incinerating in a muffle, at not below 900° C., sulphates are mostly

decomposed and fairly accurate results may be obtained without any correction. An example is given of a coke containing 0·1% CO_2 as carbonate, 0·08% S as sulphide, 0·14% Fe as sulphide, 0·82% FeO, 0·08% SO_3, and 12·76% of silicates, making altogether 13·98% of mineral matter. The ash-content found by incineration at 750° C. was 14·36% ; at 900° C., 14·13% ; and over a naked flame, 14·67%. (Cp. Wagener, this J., 1913, 935).—J. H. L.

Peat; Utilisation of ——, *in Italy* [*production of ammonium sulphate*]. U. Rossi. Monthly Bull. Agric. Intelligence, Rome. J. Roy. Soc. Arts, 1915, **63**, 162—163.
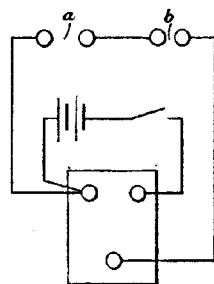
AT Orentano and Codigoro, artificially dried peat, containing 25% of water, is carbonised in a turret-shaped oven, 26—33 ft. high, by the Mond process. From 1 ton of peat containing 2·5% N about 175 lb. of ammonium sulphate are thus obtained at a cost of from 4s. 10d. to 5s. 7d. per cwt. The factory at Orentano has been working since 1910, the present daily capacity being 1800 cub. ft. of peat, yielding 50 tons of ammonium sulphate per month ; at the works at Codigoro, operated since 1912, 150 tons of dried peat, yielding 10—12 tons of ammonium sulphate, are treated daily.
—W. E. F. P.

Measuring flame velocities in gas and dust explosions; An instrument for ——. J. D. Morgan. Engineering, Jan. 8, 1915, 39—40.

ADVANTAGE is taken of the reduction in the resistance of air or gas to the passage of an electric spark caused by the rise in temperature which

takes place as the flame of the explosion moves along. Two spark gaps, *a, b*, are arranged in the circuit of wires from an induction coil. Under normal conditions a spark will not jump the wider gap, *a*, but if the resistance of the air at *a* be lowered, owing to rise of temperature, and a spark passes, a spark will also pass at *b*. The gap, *a*, is placed in the path of the explosion wave, and the gap, *b*, is arranged in conjunction with a drum carrying a band of smoked paper on which the spark will make a record. The time of rotation of the drum is registered on the paper by a line of marks made by the vibrations of a tuning fork of known periodicity. The sparking plug which fires the explosive mixture is also in series with a second spark gap, and the spark produced at the latter makes a record on the drum. The distance between the firing point and the position of the recording gap, *a*, being known, and the time interval between the firing spark record and the record corresponding to the spark produced at *a* being obtained from the tuning fork record, the time taken by the flame to travel the distance can be calculated. Several recording gaps are arranged one after the other in the path of the flame, and all register on the same drum.—W. H. C.

Coal-gas; Determination of hydrogen sulphide in ——. A. B. Way. Amer. Gas Institute. J. Gas Lighting, 1914, **123**, 660—661.

A WIDE-MOUTHED bottle of about ½ gallon capacity is fitted with a three-hole rubber stopper, which is always inserted to the same depth. A thermometer passes through one hole, and glass inlet and

outlet tubes, provided with rubber connections and pinch cocks, through the others. Gas to be tested is passed through the bottle to expel the air, and the outlet cock is closed to ensure a pressure in the bottle, which is brought to the normal, when the sample has cooled, by opening one of the pinch-cocks while the loose end of the rubber tube is immersed in water to a depth of ¼ inch. The cock is closed, the tube connected with a levelling bottle, and the other tube with a burette containing a solution prepared by dissolving 20 grms. of cadmium chloride in 125 c.c. of water and 50 c.c. of strong ammonia, filtering and making up to 1 litre with 300 c.c. of strong ammonia and water. By means of the levelling bottle about 30 c.c. of the solution are drawn into the gas bottle, and the burette and levelling bottle are disconnected. After shaking, the pressure is released by slowly opening the pinch-cock, and the contents of the bottle are poured on to a dry filter and washed with water. The filter and precipitate are placed in the bottle, an excess of $N/20$ iodine solution, 3 c.c. of starch solution, about 200 c.c. of water, and 50 c.c. of commercial hydrochloric acid are added, the stopper is inserted, the bottle shaken for a minute or two, and the excess of iodine titrated with $N/20$ thiosulphate solution. Using $N/20$ iodine and a bottle holding 2000 c.c., 1 c.c. of iodine solution represents 18·62 grains of H_2S per 100 cubic feet of gas.—W. C. H.

Natural gas as an economic mineral; Inflammable ——. J. A. L. and W. H. Henderson. Inst. Min. and Met., Jan. 21, 1915. [Advance proof.]

STATISTICS and graphs are given showing the rapid rise of the natural gas industry, particularly in the United States, which produces 97% of the world's supply. In 1912 the production in liquid volume was 85% of that of petroleum, in weight 41%, and in value 52%. The average price was 7·52d. per 1000 cub. ft. "Dry" gas, consisting mainly of methane (50—95%) with smaller quantities of ethane, propane, and butane, has an average calorific value of about 1100 B.Th.U. per cub. ft., weight 48 lb. per 1000 cub. ft., and sp. gr. 0·63 (air=1). Its production was 263% of the volume of manufactured gas and its average price was 21·5% of that of the latter. It is the most efficient fuel known for nearly all purposes, its principal limitation being the restriction of its use to the area which can be supplied by pipe line. "Wet" gas from the oil wells contains a larger proportion of heavier gases such as ethane, propane, butane, and sometimes ethylenes, its chief value being its gasolene content. Four commercial products are obtained, viz., ordinary motor spirit; the light product which is mixed with naphthas to produce motor spirit; semi-liquid "gasol," distributed in high-pressure containers; and residual "dry" gas. Very large quantities of gas have been and are still being wasted.
—W. F. F.

Petroliferous mounds of Texas and Louisiana; Origin of the ——. J. Chautard. Comptes rend., 1915, 160, 69—72.

THE following geological changes are suggested as an explanation of the formation of the petroliferous mounds of Texas and Louisiana :— Sedimentation in an intermittent lagoon of various salt formations, sands, and clays with buried organic débris, and layers of anhydrite corresponding to the periodical drying up of the lagoon; decomposition into hydrocarbons of the organic matter buried in the saline sediments : transformation of the anhydrite into gypsum, with concomitant increase in volume, causing the upper layers to be elevated into the form of mounds; migration of the petroleum under the

influence of the pressure exerted on their parent rocks, whereby eventually it is concentrated beneath the impermeable exterior of the mounds.
—G. F. M.

Oils from peat. Perkin. See IIB.

Fireclay goods and their use in gas works. Holgate. See VIII.

PATENTS.

Gas in the atmosphere of mines; Means for detecting, indicating, and recording the presence and proportions of ——. H. R. Webster, Horsforth, Yorks. Eng. Pat. 29,094, Dec. 17, 1913.

IN apparatus of the type in which the presence of firedamp is detected by diffusion through a porous vessel and the distension of a diaphragm, the movements of a rod connected to the diaphragm are multiplied by toothed gearing or other mechanical device and indicated or recorded by a pointer. The casing carrying the multiplying and indicating device is connected with the base piece carrying the porous vessel in such a way that the two parts can be moved towards or away from each other in order to bring the pointer to the zero mark.
—W. F. F.

Vertical retorts. Means for charging vertical retorts. A. Waddell, Dunfermline, Fife. Eng. Pats. (A) 6112 and (B) 6113, Mar. 10, 1914.

(A) THE partition dividing a pair of retorts extends nearly to the crown of a single arch which forms their common floor, and which has an inclination almost sufficient to discharge the coke by gravity. A curved pusher resting on the arch is reciprocated from one retort to the other by rack and pinion gear; or a single retort may have a plane sloping floor, with a pusher travelling parallel to it. (B) To charge the retort with minimum loss of gas, the coal bogie has within it a discharging sleeve movable vertically, which is lowered on to a ring supported on the usual conical valve of the retort. On lowering the valve the sleeve descends with it and rests on the mouth of the retort, thus preventing lateral escape of gas.—W. F. F.

Coke; Method of cooling ——. Wärme-Verwertungs-Ges. m. b. H. Ger. Pat. 276,982, Aug. 19, 1913.

THE coke is cooled dry in jacketed chambers, water being circulated through the jackets at a high velocity and under such pressure that no evolution of steam occurs. The same water is used to absorb waste heat from all other sources in the coking installation, and a chamber is interposed in the circuit, in which a lower pressure prevails, and in which steam is evolved.—A. S.

Producer gas; Process and arrangement of plant for the treatment and recovery of tar and ammonia liquor from ——. Q. Moore, Glasgow, and The Dowson and Mason Gas Plant Co., Ltd., Manchester. Eng. Pat. 2650, Feb. 2, 1914.

THE gas is cooled to 100°—160° F. (38°—71° C.) in an air-cooled condenser and passed through a tar-extractor and second air-cooled condenser at a higher level. The tar and condensed liquor from the extractor and second condenser flow back through the first condenser in the reverse direction to the hot gas, whereby the tar is dehydrated. The tar and ammonia liquor are separated by decantation, and the latter is passed first through a heat exchanger, where it heats the water for the producer jacket, and then through a scrubber in the reverse direction to the gas from the second condenser. A strong ammonia solution is thus obtained.—W. F. F.

Petroleum-distilling apparatus. Process for distilling petroleum. R. E. Humphreys, Assignor to Standard Oil Co., Whiting, Ind. U.S. Pats. (A) 1,122,002, and (B) 1,122,003, Dec. 22, 1914. Dates of appl., June 14, 1913, and Jan. 20, 1914.

(A) IN a horizontal cylindrical still, the liquid is circulated between curved plates arranged substantially parallel to the still bottom, and each formed in two sections. The outer edges of the sections are hinged at opposite ends of a horizontal diameter of the still, and the inner, lower edges are detachably hooked together. (B) The above apparatus is used for treating paraffins from petroleum distillation boiling above 500° F. (260° C.), to obtain products of lower boiling point, by heating at 650°—850° F. (343°—454° C.), and a pressure above 4 atmospheres in contact with catalytic metal plates, and condensing only a small fraction.—W. F. F.

Gasoline; Means for controlling still-pressure in manufacture of ——. F. M. Rogers and T. S. Cooke, Assignors to Standard Oil Co., Whiting, Ind. U.S. Pat. 1,122,220, Dec. 22, 1914. Date of appl., Aug. 5, 1914.

Two gas-discharge pipes are provided, one slightly smaller than necessary to maintain the desired pressure alone, and the other of small capacity and provided with a valve operated by the pressure in the still, so that it releases separate measured quantities of gas.—W. F. F.

Cooling hot or molten fats and fatty emulsions and the like. Eng. Pat. 10,863. *See* XII.

Water purification. [*Removing gasoline, etc.*]. U.S. Pat. 1,121,994. *See* XIXB.

IIB.—DESTRUCTIVE DISTILLATION; HEATING; LIGHTING.

Peat; Oils from ——. F. M. Perkin. J. Inst. Petroleum Technologists, 1914, **1**, 76—84.

THE destructive distillation of dry peat yields a thick tar containing paraffin wax, and an aqueous distillate containing ammonia, acetic acid, acetone, and methyl alcohol. The gases evolved are sufficient to carbonise the peat if it has been previously dried till it contains only 20% H_2O. Coke hard enough for metallurgical purposes is obtained from suitably dried briquetted peat. The tar is fractionated, finally with superheated steam, to prevent carbonisation, and the fractions are washed with alkali and acid. The oils are largely paraffinoid. The yield from a briquetted Yorkshire peat was 38 galls. per ton, giving on fractionation 1·35% of oil of sp. gr. 0·867 below 150° C., 29·90% of sp. gr. 0·953 below 250° C., 50·00% of sp. gr. 0·941 above 250° C., and a residue of hard pitch. The last fraction contained 6% of paraffin wax. From 11 to 22 lb. of ammonium sulphate per ton· was also obtained. The cost of dried peat should not exceed 4s. 6d. per ton, and on this basis the production of oil and carbon should be remunerative. Details of a plant to treat 50 tons of wet peat per day show that the capital required is £3070, and the labour charges £748 16s. for 6 months. Labour charges would be lower for a larger plant. (See also this J., 1914, 395.)—O. E. M.

Hardwood distillation industry in America. E. H. French and J. R. Withrow. Amer. Inst. Chem. Eng., Dec. 4, 1914. Met. and Chem. Eng., 1915, **13**, 30—39.

A HISTORY of the development of the industry is given, and the various methods of distillation in use and the design and construction of the apparatus are considered in relation to the yields and production costs of crude wood-alcohol, acetate of lime, and charcoal. In the most successful and modern system, the wood is carbonised in ovens (width 6 ft. 3 in., height 8 ft. 4 in., length 26—54 ft.; capacity 5—10 cords of 52 in. wood), to which tubular condensers are attached. The products obtained per cord (about 2 tons) of average, seasoned wood are :—crude liquor (containing 8—8·5% of acid and 4—4·5% of alcohol), 215—220 galls. ; tar, 22—25 galls. ; charcoal, 52 bushels (1040 lb.) ; and gas, 11,000—12,000 cub. ft., the latter consisting largely of air and carbon dioxide in the early stages, but having an important fuel value from the middle to the end of the distillation. The yields are greatly influenced by the manner in which the carbonisation is conducted, too high a temperature at the height of the run (above 750° F. [399° C.] at the neck of the oven) resulting in the formation of excessive quantities of non-condensable gases and tar, to the detriment of the more valuable products. The final products obtained are :—wood-alcohol (82%), 11 galls., value $2.75 (11s. 5½d.) ; acetate of lime, 216 lb., value $3.78 (15s. 9d.) ; charcoal, 52 bushels, value $3.38 (14s. 1d.) ; total value $9.91 (41s. 3½d.) as against a total production cost of $8.85 (36s. 10½d.) per cord. For an oven plant operating on the above lines the cost of installation is about $2000 (about £420) per cord per day capacity. In the United States there are, at the present time, 53 oven-, 31 retort-, and 6 kiln-plants having total daily capacities of 2909, 593, and 1300 cords, respectively ; and in Canada, 1 retort- and 9 oven-plants having total daily capacities of 48 and 424 cords respectively. The annual production of crude wood alcohol in America is between 10 and 11 million gallons.

—W. E. F. P.

Flaming arc carbons; Chemistry of ——. W. C. Moore. Amer. Electrochem. Soc., Nov., 1914. Met. and Chem. Eng., 1915, **13**, 52—55.

THE chief constituents of flaming arc carbons for yellow and white light (those most commonly employed) are calcium fluoride and rare-earth compounds, respectively ; but smaller proportions of other constituents or " addition agents " (usually three or more) are also present. All materials should be free from silica, ferric oxide, alumina, and similar impurities which, by promoting the formation of slag or non-volatile compounds would cause poor or irregular burning. Other factors being equal, the candle power developed is dependent on the amount of flame material and the proportions of the addition agents present : the following comparative results were obtained with cored carbons :—

Parts of calcium fluoride by weight	3	2	1	0
Parts of other salt by weight	0	1	2	3
Mean spherical candle power	927	1058	765	574

H. P. Gage (Phys. Rev., 1911, **33**, 111) found that with cored yellow-flame and white-flame carbons the energy radiated as light from the arc stream was 39 and 27·5%, respectively, of the total radiant energy, these values being for the spectral region between 3800 and 6800 Ångström units and an alternating current at 13·5 amp. In general, flaming arcs are of two types, according as the sheath or the core of the carbon appears the more luminous ; an arc of the first kind is obtained with carbons containing calcium fluoride, and of the second with carbons containing chromic oxide : with few exceptions, arcs of the latter type give light of shorter wave-length.—W. E. F. P.

Translucent marble for lamps. Voege. *See* VIII.

PATENT.

Charcoal; Manufacture of decolorising —— from vegetable materials impregnated with salts before carbonisation. C. G. Hanhart. Ger. Pat. 275,973, Aug. 19, 1913.

THE vegetable material is impregnated with an easily soluble salt, such as calcium or magnesium chloride, then carbonised in presence of air at a comparatively low temperature, and the salts removed from the charcoal by lixiviation.—A. S.

III.—TAR AND TAR PRODUCTS.

Benzol; Sale and export of ——. Modification of test. J. Gas Lighting, 1915, **129**, 198.

IF 95% of the sample distils below 90° C. instead of below 84° C. as previously specified (see this J., 1915, 21), the sample may be sold without permit.
—W. H. C.

PATENT.

Acenaphthene; Process for obtaining —— from coal tar oils. Ges. f. Teerverwertung m. b. H. Ger. Pat. 277,110, Nov. 8, 1913.

WHEN heavy coal-tar oil is submitted to fractional distillation, a mixture of acenaphthene and other substances crystallises from the after-runnings of the acenaphthene fraction. According to the present patent this is mixed with some of the liquid distillate between the naphthalene and acenaphthene fractions and again distilled to recover the acenaphthene.—A. S.

IV.—COLOURING MATTERS AND DYES.

National dye scheme. Board of Trade Announcement, Jan. 29, 1915 (see also this J., 1915, 73).

THE provisional committee of users of dyes, which has been appointed to confer with the Board of Trade as to a scheme for the establishment of a national dye-making industry on a large scale, met on January 27th and 28th at the Board of Trade offices. The members of the enlarged Committee are :—Sir A. F. Firth, Bt., Sir Frank Hollins, Bt., Sir Mark Oldroyd, Mr. H. W. Christie, Mr. J. Clarkson, Mr. Charles Diamond, Mr. Kenneth Lee, Mr. G. Marchetti, and Mr. R. D. Pullar.

The Committee eventually came to a unanimous decision in favour of the adoption of a modified scheme, which it is believed will be acceptable to the various interests concerned. The full details of the scheme adopted will be made public after a further meeting of the Committee has been held, but it is now possible to indicate its general lines, which differ in certain important respects from those of the scheme already made public.

The proposal is to form a company with an initial share capital of £2,000,000, of which £1,000,000 will be issued in the first instance. The Government will make to the company a loan for 25 years amounting to £1 for every £1 of share capital subscribed up to a total of £1,000,000, and beyond that, £1 (up to a maximum sum of £500,000) for every £4 of share capital subscribed. The Government advance will bear interest at 4% per annum payable only out of net profits, the interest to be cumulative only after the first five years. There will be no compulsory sinking fund, but the dividend on the shares will be

limited to 6% per annum on the paid up share capital so long as any part of the Government's advance is outstanding.

In addition, and with the desire of promoting research, the Government have undertaken for a period of 10 years to make a grant to the company for the purposes of experimental and laboratory work up to an amount not exceeding in the aggregate £100,000.

With the object of securing that the company shall remain British and of preventing undue preference or encroachment on the businesses of British manufacturers of products other than dyes and colours, the Government will nominate two directors of the Company with special powers in relation to these matters. There is, however, no intention of using these powers to prevent the company from giving priority to shareholders in the supply of dyes or from making the by-products incidental to the manufacture of dyes.

The terms of the proposed agreement to be entered into between users of dyes and the company have been considerably modified in favour of the users.

An option has already been obtained for the acquisition of important dye-making works and negotiations for other options of a like character are in progress, whilst there is reason to believe that arrangements satisfactory to both parties can be made with important producers in Switzerland. Early steps will be taken to develop the supply of dyes both by the enlargement of the plants of the undertakings acquired and in other ways.

It is proposed that the company shall take powers to arrange for the assistance of a committee of experts conversant with the dyeing trade and its requirements, and in this connection Lord Moulton has promised to give the company the benefit of his assistance and advice.

It is believed that the steps thus taken will provide for the full and immediate utilisation of available resources for the manufacture of dye-stuffs and will provide an organisation capable of expansion so as to deal with the problem on a more comprehensive scale.

Dyestuffs in the United States; Proposed manufacture of ——. Board of Trade J., Jan. 21, 1915.

THE Benzol Products Company of Philadelphia, which is connected with an important company manufacturing coal-tar products and said to be supported by a capital exceeding 100,000,000 dols. (about £20,550,000), has purchased seventy-five acres of land at Marcus Hook, Delaware Co., Pa., with a view to erecting large modern factories for the production of coal-tar dyes. Two thousand workmen, it is stated, will be employed, and it is estimated that production will commence in about six months' time.

• V.—FIBRES ; TEXTILES ; CELLULOSE ; PAPER.

" Kemps " [in wool]. H. Priestman. J. Soc. Dyers and Col., 1915, **31**, 5—8.

PHOTOGRAPHS of a " kemp " show that the medulla is composed of approximately spherical cells which, through some peculiarity of growth, take the place of the spindle-shaped cells of the normal wool-fibre. These spherical cells occupy the same volume as the normal medullary cells, making the kemp fibre about one-fourth the length and twice the diameter of the normal fibre. The opacity of a " kemp " is an optical effect of refraction and the kemp becomes transparent when saturated with a liquid such as benzine.

" Flat kemps " owe their curious lustre and opacity to the fact that they are collapsed hollow tubes. It is not certain whether the internal cells are completely missing, as has been suggested, but if they are present, they are entirely modified and contracted in size, leaving a hollow air-space. The latter view is supported by the fact that in certain processes of black dyeing the fibre swells out again, apparently through the expansion of some substance on the interior wall of the tube. In many cases normal internal cells are visible at the root-end in the form of a tuft, with the appearance of having been pushed out of the tube by pressure ; this is the only direct evidence that " flat kemps " have at one time contained normal spindle-shaped cells.—J. F. B.

Acetylcelluloses. E. Knoevenagel. Verein deutscher Chemiker, June, 1914. Z. angew. Chem., 1914, **27,** 505—509.

ACETYLCELLULOSES are now made exclusively by the action of acetic anhydride on cellulose in presence of a catalyst, the use of acetyl chloride having been abandoned. Many catalysts, especially sulphuric acid, induce acetolysis of the cellulose molecule, a process quite distinct from hydrolysis and leading ultimately to the transformation of the cellulose into cellobiose octa-acetate and dextrose penta-acetate (see also this J., 1914, 102). Earlier methods of preparing acetone-soluble acetylcelluloses proved unsatisfactory because they involved decomposition of the cellulose molecule by hydrolysis or saponification and hence yielded products which gave solutions of low viscosity. A series of investigations in the author's laboratory has shown that by heating acetylcelluloses insoluble in acetone with ethyl acetate, benzene, acetone, alcohol, amyl alcohol, acetic acid, ethylene bromide, acetylene tetra-chloride, cyclohexanone, etc., easily soluble acetylcelluloses can be obtained without any appreciable hydrolysis or saponification of the cellulose molecule. The transformation is accelerated by a small quantity of water and by neutral and acid salts, *e.g.,* sodium ethylsulphate, methylamine bisulphate, zinc chloride, ammonium nitrate, aniline salts. The soluble acetylcelluloses prepared in this way are stated to possess more valuable qualities than those obtained by other methods. The changes are attributed to intra-molecular transformation of the cellulose acetate.
—A. S.

Wood ; Formation of furfural in the steaming of ——. E. Heuser. Z. angew. Chem., 1914, **27,** 654—655.

THE furfural produced in the steaming of wood or straw under 4 atmos. pressure (this J., 1914, 856) is formed from the pentosans. No formation of furfural, however, occurs on boiling with water or steaming at the ordinary pressure, even with the addition of acetic or formic acid. The effect of varying conditions was studied in the case of xylose. When an aqueous solution of this pentose (0·41 grm. in 60 c.c.) was heated in a sealed tube at 135°—140° C. for 8 hours, the furfural produced amounted to 11·70% of the weight of xylose. Under the same conditions, with the addition of 8 c.c. of 10% acetic acid and 4 c.c. of 10% formic acid, the yield of furfural was increased to 31·32%. Still higher yields were obtained by increasing the temperature or the concentration of the organic acids.—J. F. B.

Nitrocellulose from cotton and wood celluloses. Schwalbe and Schrimpf. *See* XXII.

PATENTS.

Drying apparatus more particularly for the treatment of textile materials. E. Feuillette, Boulogn sur Seine, France. Eng. Pat. 29,774, Dec. 24 1913. Under Int. Conv., Jan. 7, 1913.

SEE U.S. Pat. 1,108,565 of 1914; this J., 1914, 1006.

Apparatus for making bisulphite liquor [*for paper making*]. U.S. Pat. 1,119,004. *See* VII.

Varnish [*for fabrics*]. Eng. Pat. 13,100. *See* XIII.

VI.—BLEACHING ; DYEING ; PRINTING ; FINISHING.

Colouring matters as the cause of tendering of fibres. P. Heermann. Chem.-Zeit., 1914, **38,** 1281—1282.

SAMPLES of raw silk, boiled-off unweighted silk, and boiled-off and weighted silk, were dyed yellow with dyestuffs containing nitro groups, picric acid, Naphthol Yellow S, and Azoflavine FF being used. Samples kept unexposed to light retained their strength and gave no reaction with diphenyl-amine and sulphuric acid, but samples exposed to light turned browner, and gave the nitric acid test with diphenylamine and sulphuric acid. Tendering occurred in all samples exposed to light, but more quickly with weighted silks than with the unweighted silks. On longer exposure to light the colour faded and further tendering occurred, and the weighted silks failed to give the nitric acid test with diphenylamine. The explanation given is the formation of a nitro-derivative of the silk fibre by nitric acid split off from the dyestuff, the nitro-derivative under the action of light being stable in the case of unweighted silk, and unstable in the case of weighted silk. In no case was the formation of a peroxide detected by means of zinc iodide-starch solution as Gebhard has suggested (see also this J., 1914, 1153).—G. H. F.

Mercerising ; A new process of ——. E. Knecht. J. Soc. Dyers and Col., 1915, **31,** 8—10.

A CONSIDERABLE mercerising effect is produced, without injury to the feel and tensile strength, by immersing cotton yarn for 30 seconds in hydro-chloric acid of 38° Tw. (sp. gr. 1·19). Stronger acids (39°—40° Tw., sp. gr. 1·195—1·2) make the fibre harsh and brittle. The mercerising effect is still considerable with hydrochloric acid of 37° Tw. (sp. gr. 1·185) but ceases with weaker acids from 36° Tw. (sp. gr. 1·18) downwards ; lowering the temperature does not increase the activity of the weaker acids. The mercerisation is accompanied by shrinkage amounting to 8% with acid of 38° Tw. and 4% with acid of 37° Tw.; the yarn becomes curly, but attempts to produce lustre on Egyptian cotton by treatment under tension were not successful. The treated cotton exhibits most of the properties of hydrated cellulose ; it is characterised by an increased affinity for substantive dyestuffs which is greater when the fibre is dyed without drying ; the microscopic appearance is not much changed.
—J. F. B.

PATENTS.

Cleansing of linen, woollen, cotton, and other goods. F. L. Bartelt, Bristol. Eng Pat. 28,500, Dec. 10, 1913.

THE material is washed, cleansed, and " nourished " by treating it with a mixture of sodium carbonate and an aqueous solution of glycerin.
—B. N.

Dyestuffs; Fixing ——— upon textile fibres. B.
Leech, Macclesfield. Eng. Pat. 29,479, Dec. 22,
1913.

THE fibres are impregnated with a suitable acid
(e.g., tannin), and then treated with a solution
of a silicate. In the case of basic dyestuffs this
treatment precedes the dyeing process, but with
indigo and other vat dyestuffs the dyed material
is treated as described.—B. N.

Dyestuffs; Application of [sulphide] ———. E. Lodge
and J. M. Evans, Huddersfield. Eng. Pat. 29,852,
Dec. 29, 1913.

IN dyeing union goods with sulphide dyestuffs,
reduction to the leuco compound is effected by
an alkali hydrosulphite in presence of an alkali
sulphite.—B. N.

Printing of textile fabrics and the like. H. Levin-
stein, and Levinstein Ltd., Manchester. Eng.
Pat. 29,359, Dec. 20, 1913.

FAST printed shades are obtained upon vegetable
fibres by printing the fabric with a paste con-
taining a non-substantive azo dyestuff capable
of forming an insoluble compound with formalde-
hyde, and subsequently treating the dyestuff
upon the fabric with formaldehyde.—B. N.

*Coating or covering fabrics with a layer of adhesive
material.* F. Stoffel, Paris. Eng. Pat. 15,262,
June 25, 1914. Under Int. Conv., Dec. 29, 1913.

ADHESIVE material, such as gelatin, in a pasty
condition, is pulverised and projected on to the
fabric by means of a blow-pipe. The material is
uniformly spread on the fabric, and is cooled,
coagulated, and almost completely dried by the
expansion of the air during pulverisation.—B. N.

*Waterproofed textile material and process of making
same.* R. A. Marr, Assignor to General Water-
proofing Co., Inc., Norfolk, Va. U.S. Pats.
(A) 1,121,647 and (B) 1,121,648, Dec. 22, 1914.
Date of appl., Jan. 13, 1914.

(A) THE textile fabric or cordage is impregnated
with an impermeable, preservative waterproofing
agent, comprising diatomaceous earth and an
insoluble, inert, hydrocarbon carrier, such as
paraffin and naphthalene, solid at ordinary
temperatures but liquid at temperatures near
the boiling point of water. (B) The water-
insoluble carrier is composed of paraffin, a dyestuff
soluble in it, and rosin, the impregnation being
carried out above 100° C., and the temperature
of the impregnating material decreased during
the process.—B. N.

VII.—ACIDS; ALKALIS; SALTS; NON-METALLIC ELEMENTS.

*Sulphuric acid; Apparatus for the concentration of
———.* W. Mason. Met. and Chem. Eng., 1915,
13, 17—18.

DETAILS are given of a "capsule" plant, com-
prising 6 lead pans and 40 capsules (basins) of fused
silica, in which 4 tons of acid (95·25% H₂SO₄)
were produced from 65% acid per 24 hours at a
cost of 6s. 4½d. per ton. The acid condensed from
the exit gases was 2·23% of the total, as against
about 15% in the glass retort system of con-
centration. The total cost of the apparatus,
including erection, is estimated at £265. With
careful and regular working an ordinary furnace
may be used, and the loss due to breaking of the
capsules thereby minimised. With a forced-draught

furnace, too high a temperature is produced
in the lower part of the plant, leading to bumping
and breaking of the capsules.—W. E. F. P.

*Boric acids in alcohol; Some properties of solutions
of the ———. A modified boiling-point apparatus.*
J. B. Firth and J. E. Myers. Chem. Soc.
Trans., 1914, 105, 2887—2892.

THE change in the boiling point of pure ethyl
alcohol, with varying quantities of orthoboric and
metaboric acids and with boron trioxide, was
determined by enclosing the ordinary Beckmann
apparatus in a Dewar vessel, and heating the
liquid electrically by means of a fine platinum
wire. With low concentrations of the sub-
stances, the boiling points of ethyl alcohol solutions
are lower than the boiling point of the pure sol-
vent. The maximum lowering is produced by the
least volatile substance, boron trioxide, and the
least with orthoboric acid, metaboric acid occupy-
ing an intermediate position. With higher con-
centrations the boiling point is raised, the least
volatile substance having the greatest effect.
—B. N.

*Cyanides, thiocyanates, ferro- and ferricyanides;
Rapid detection of ——— in mixtures.* F. Feigl.
Chem.-Zeit., 1914, 38, 1265.

SOLUTIONS to be tested are treated with an excess
of zinc nitrate, warmed, and filtered. Thio-
cyanates remain in the filtrate, and cyanides, ferro-
cyanides and ferricyanides can be detected in the
washed precipitate by spot tests made on filter-
paper with small quantities of the precipitate and
strongly acid solutions of mercurous, ferric, and
ferrous (free from ferric) salts respectively. The
tests are not affected by the presence of fluorides,
phosphates, borates, sulphates, chlorides, bromides,
iodides, chlorates, carbonates, nitrates, or silica,
but chromates and ammonium salts must first be
removed. In presence of borates, mercurous salts
produce a green coloration which cannot be con-
fused with the black colour given by cyanides.
The test with mercurous salts is useless in presence
of sulphides, sulphites, or compounds which reduce
the reagent. In such cases cyanides may be
detected by warming gently some of the washed
zinc precipitate with dilute sulphuric acid in a
porcelain crucible covered with filter-paper moist-
ened with ammonium sulphide solution, and after-
wards testing the paper for thiocyanates by means
of acid ferric chloride solution.—J. H. L.

Tri-ammonium citrate. R. A. Hall. J. Amer.
Chem. Soc., 1915, 37, 208—216.

TRI-AMMONIUM citrate, (NH₄)₃C₆H₅O₇, is obtained
quantitatively when dry ammonia is passed into
a boiling absolute alcoholic solution of citric acid.
It is stable, crystalline, very soluble in water, and
alkaline towards rosolic acid. A solution of sp. gr.
1·09 at 20° C. is recommended for use in phosphoric
acid determinations in place of " neutral " am-
monium citrate solution.—J. R.

*Lead oxide; Determination of peroxide in com-
mercial ———.* L. S. Dean. Chem. News, 1915,
111, 2.

THE peroxide is decomposed with hydrochloric
acid in presence of potassium iodide, using carbon
tetrachloride or chloroform as indicator, the excess
of potassium iodide being titrated with standard
potassium iodate solution: 2PbO₂ = KIO₃ (cf.
L. W. Andrews, J. Amer. Chem. Soc., 1903, 23,
792). The method is as accurate as Bunsen's
method and possesses the advantages that small
quantities of peroxide can be estimated in presence
of organic matter, no special apparatus is needed,
and larger amounts of substance, e.g., litharge,

can be used, as the whole of the oxide need not be dissolved.—R. G. P.

Rare earths ; The electrolysis of solutions of the ——. L. M. Dennis and B. J. Lemon. J. Amer. Chem. Soc., 1915, **37**, 131—137.

THE solutions were electrolysed in a glass cell, 12 cm. in diam. and 13 cm. high, the cathode being a 3 cm. layer of mercury and the anode a platinum wire of 0·76 mm. diam. The surface of the cathode was kept clean by violent agitation with an air current. With an E.M.F. of 9 volts a fairly rapid precipitation of hydroxides occurred from a neutral solution of the nitrates of neodymium, praseodymium, lanthanum, and samarium containing 50 grms. of the oxides per litre. Fractions of the hydroxides filtered off at intervals of 5 or 6 hours showed a gradual decline in atomic weight from 140·9 to 138·9. This method when applied to a mixture of the nitrates of praseodymium and lanthanum resulted in a fairly rapid concentration of lanthanum in the solution ; and fractional electrolysis of a mixture of earths from xenotime effected a similar concentration of yttrium in the solution, while the first three fractions of precipitate were rich in erbium. The process may in certain cases be preferable to fractional crystallisation or precipitation.—J. R.

Hydrogen and chlorine ; Interaction of ——, under the influence of the alpha particles. H. S. Taylor. J. Amer. Chem. Soc., 1915, **37**, 24—38.

THE combination of hydrogen and chlorine under the influence of the α-particles from radium emanation is a reaction of the first order and is analogous to the corresponding photochemical reaction.—J. R.

Heavy chemicals. Board of Trade Bulletin No. 67.

THE following statement shows for a recent year the value of the under-mentioned heavy chemicals exported from Germany, Austria-Hungary, and the United Kingdom, respectively, to all destinations :—

Description.	From Germany (1912).	From Austria-Hungary (1913).	From United Kingdom (1913).
	£	£	£
Aluminous sulphates (including alums)	390,400	3,945	77,400
Arsenic and its oxides and compounds	56,400	—	13,500
Bleaching materials	245,800	11,900	168,600
Coal products, not dyes :			
Carbonate of ammonia	5,800	1,000	132,300
Aniline oil and aniline salts	628,400	130	28,900
Benzol, toluol, etc.	342,500	—	302,800
Carbolic acid (including phenol)	194,100	8,250	190,500
Coal tar	163,300	3,850	84,900
Naphthalene	44,300	7,750	37,700
Pitch	183,200	78,600	1,100,000
Anthracene, creosote and other tar oils	360,500	—	592,400
Copper sulphate	87,100	4,100	1,701,200
Potassium or sodium cyanide	472,000	—	562,200
Soda compounds :			
Soda ash	319,900	12,100	563,300
Sodium bicarbonate	18,400	175	123,600
Caustic soda	125,700	80	723,700
Sodium chromate and bichromate	77,600	100	59,900
Soda, raw and crystallised	6,000	800	45,300
Sodium sulphate	158,800	3,785	114,000
Sulphuric acid	186,400	28,000	62,700
Total	4,066,600	164,565	6,684,900

The following statement shows for the year 1912 the value of the under-mentioned heavy chemicals exported to the United Kingdom from Germany

side by side with the production in the United Kingdom in 1907 :—

Description.	German Exports to United Kingdom (1912).	Produced in the United Kingdom in 1907.
	£	£
Aluminous sulphates (including alums) ..	83,900	216,000
Arsenious acid, arsenic acid, and arsenic compounds	3,000	55,000
Bleaching materials	44,600	527,000
Coal products not dyes :		
Carbonate of ammonia	850	132,300*
Aniline oil and aniline salts, etc.	51,800	28,900*
Benzol, toluol, etc.	2,700	189,000
Carbolic acid (including phenol and cresol)	8,300	216,000
Coal tar	250	911,000
Naphthalene	1,900	45,000
Mineral pitch	—	859,000
Anthracene, creosote, and other tar oils	3,200	712,000
Copper sulphate	400	1,540,000
Potassium or sodium cyanide	12,700	562,200*
Soda compounds :		
Soda calcined, bleaching soda, etc. ..	250	
Bicarbonate	3,400	
Caustic soda, solid or liquid	3,100	3,390,000
Soda, raw and crystallised	150	
Sulphate and bisulphate	1,800	
Chromate and bichromate	31,600	59,900*
Sulphuric acid	1,200	955,000
Total	£255,100	£10,407,300

* Exports only.

It is thus clear that in these particular lines British manufacturers have no need to fear German competition in the home market.

Germany's principal markets for alums are Switzerland, France, Netherlands, Belgium, United States, Sweden, Spain, Italy, and Argentina, and in those markets, with the exception of the United States and Argentina—where the United Kingdom does a fair trade—Germany has hitherto held a very strong position, but there would appear to be openings for the sale of British-made alums in all these countries.

German exports of arsenic compounds are about four times those of the United Kingdom. The principal market for both countries is the United States, the larger share, however, falling to Germany. In Italy the United Kingdom does a somewhat larger trade than Germany, but elsewhere, porticularly in Scandinavia, France, Russia, Brazil, Uruguay, Dutch East Indies, and Argentina the German product has the larger sale. There should be possibilities of extending the sales of British-made arsenic compounds in several of these markets. British exports of bleaching powder to the principal Colonial and neutral markets are only slightly smaller than those of Germany. The principal market for both countries is the United States, the advantage lying with the United Kingdom. In Denmark, British India, China, and Brazil we hold strong positions, but elsewhere the bulk of the trade falls to Germany, though fair amounts are supplied by the United Kingdom to the Netherlands and Russia. The United Kingdom has practically the whole of the export trade in carbonate of ammonia to the principal Colonial and neutral markets, though there is a certain amount of German competition in Italy and Switzerland, and in the South American markets.

Germany does the bulk of the export trade in aniline oil and toluidine, and there appear to be openings for the British-made article in the United States, Switzerland, Italy, Russia, Spain, Belgium, Netherlands, Turkey, and Japan. The bulk of the benzol and toluol exported from both Germany and the United Kingdom is sent to France. In

present circumstances there would appear to be exceptional opportunities for extending the sale of British-made benzol and tolnol in that market. Openings also exist in the Belgian, Dutch, Italian, Swiss, Russian, Argentine, and United States markets, though the possibilities in these markets are much smaller. The exports of carbolic acid from Germany to the principal colonial and neutral markets are slightly larger in the aggregate than those of the United Kingdom. The distribution, however, varies considerably. Thus the United Kingdom supplies the bulk of the carbolic acid required in British India, Sweden, and Netherlands; Germany, on the other hand, has hitherto taken the lead in supplying the French, Swiss, Russian, and Japanese markets. In the United States market the United Kingdom and Germany up to the present have shared the market about equally. Valuable openings for the sale of carbolic acid would appear to exist in France, Italy, Switzerland, Russia, Japan, and the United States. The United Kingdom already holds the bulk of the coal tar trade with British India, British South and West Africa, and Australia, while Germany holds a long lead in the Belgian, French, and Russian markets, which at the moment offer considerable openings for the supply of British-made coal tar. Naphthalene is a small trade. The United Kingdom does the bulk of the business with British South Africa, Netherlands, and Italy. Germany takes the lead in Sweden, Denmark, Belgium, Switzerland, Russia, and Turkey, while the United Kingdom and Germany roughly divide the trade with France, China, and the United States fairly equally between them. There should be a number of small openings in the markets mentioned. In some of the smaller markets, e.g., Netherlands, Switzerland, and Turkey, the larger portion of the pitch imported comes from Germany, but in the larger markets, although Germany does a fair trade, the United Kingdom holds a far stronger position than Germany. This is particularly the case in Belgium, France, Russia, and Egypt. Over 90% of the United Kingdom exports of tar oil, creosote, etc., are sent to the United States, where there is not very much competition from German tar oil. On the other hand Germany sent nearly one-half her total exports of tar oil to the Netherlands, Belgium, and France, to which markets British exports of tar oil are relatively small. Both the United Kingdom and Germany do a fair trade with Canada, Norway, Sweden, Italy, Russia, and Brazil, but in Switzerland and Roumania the British product is unrepresented, the whole of the trade going to Germany.

Germany has only a very small export trade in copper sulphate. Her two largest markets, Switzerland and Servia, are the only ones to which the United Kingdom does not export this substance. Germany has a firm grip on the United States cyanide market, and also supplies larger quantities than the United Kingdom to British South Africa, Mexico, Russia, Spain, and Italy, whilst the Dutch East Indies, Switzerland, Belgium, and the Netherlands, were not supplied with any of this chemical by the United Kingdom in 1913. The United Kingdom exports of soda ash are greater than the exports of "soda calcined, refined; bleaching soda, etc," from Germany, but the markets supplied by the United Kingdom are quite different from those supplied by Germany. Thus, though the United Kingdom practically controls the distant markets of Japan, British India, Argentina, Brazil, United States, Russia, Dutch East Indies, and Chile, Germany has very little competition from the United Kingdom in European markets, e.g., Belgium, Switzerland, Sweden, Norway, and Denmark. There is also room for extension of the United Kingdom trade with Netherlands and Italy.

The United Kingdom exports considerably more sodium bicarbonate than Germany, though our present trade might be extended in the Swedish, Danish, Belgian, Dutch, Swiss, and Russian markets. More than 60% of Germany's total exports of caustic soda in 1912 went to Switzerland, whereas in this market the United Kingdom was quite unrepresented as regards this commodity in 1913. In all other markets the United Kingdom export trade exceeds the German, except in the case of Belgium. The countries which offer the greatest scope for British enterprise in this trade, in addition to Switzerland and Belgium, are Italy, Roumania, Scandinavia, the Netherlands, and Russia. The greater part of the export trade of both Germany and the United Kingdom in sodium chromate and bichromate is with Western Europe (France, Netherlands, Switzerland, Belgium, and Spain). In all of these markets Germany has, so far, had the major portion of the trade, and it would seem that there is ample opportunity for British traders to increase their exports to these markets. The United States also was largely supplied with this chemical by Germany, and German trade to the value of £2,000 with British possessions might be secured by British exporters. Soda crystals is a small trade, and one in which the United Kingdom does more export trade than Germany. There are, however, a few markets which might be captured from Germany in the present circumstances, viz., Switzerland, Russia, France, and Belgium, whilst extensions might be made in the case of the Netherlands, Brazil, Chile, and the United States. There is a large market for sodium sulphate in Belgium and the Netherlands, the exports from Germany to these two countries being about 3½ times as great as the exports from the United Kingdom. In the United States, Brazil, Italy, France, and Denmark, German exports are greater than British, whilst the United Kingdom sent none of this commodity to Switzerland, Roumania, Venezuela, and Mexico in 1913. The export trade in sulphuric acid to most of the neutral markets specified was almost entirely in German hands. In present circumstances an appreciable share of the trade might now be obtained by British manufacturers of sulphuric acid.

Austria's exports of heavy chemicals are insignificant compared with those of Germany and the United Kingdom. Her principal markets are Roumania (for chloride of lime, carbolic acid, naphthalene, calcined soda, and sulphuric acid); Russia (for coal tar and pitch); Italy (for coal tar pitch); Servia (for coal tar and pitch, copper sulphate, and calcined soda); and Bulgaria (for carbolic acid and naphthalene).

The ternary system, CaO–Al$_2$O$_3$–SiO$_2$. Rankin and Wright. *See* IX.

Use of titanous chloride in quantitative analysis. Monnier. *See* XXIII.

.PATENTS.

Bicarbonate of soda; Production of ——. C. White, London. Eng. Pat. 21,546, Sept. 24, 1913.

A SOLUTION of magnesium bicarbonate and chloride is treated with sodium chloride and carbon dioxide, under such conditions that the liquor remains approximately saturated with magnesium chloride. For example, magnesium oxide, hydroxide, or carbonate, mixed with water, is treated with carbon dioxide under pressure, the solution is saturated with magnesium chloride, a concentrated solution of sodium chloride added, and carbon dioxide again introduced under pressure; the precipitated sodium bicarbonate is then separated and the residual solution treated with

magnesium oxide, etc., to prepare a further quantity of magnesium bicarbonate solution, and so on.—F. SODN.

Salt; Apparatus for the manufacture of ——. J. W. Stubbs and J. Hollins, Middlewich. Eng. Pat. 28,469, Dec. 10, 1913.

A BRINE evaporating vessel having vertical evaporating tubes is constructed with external circulating downcomers from the upper to the lower chamber, these downcomers having a long flat cross-section which decreases from the top downwards, so as to present a large cooling surface and also secure an effectual precipitation of salt in the bottom of the lower chamber. A firebrick casing, communicating with a furnace, surrounds the evaporating tubes, a central passage between the tubes serving for cleaning purposes, and each tube-plate is protected from the heat by an adjacent loosely fitting false tube-plate. Vessels are arranged in series with communicating flues, and a by-pass flue, with dampers, allows any vessel to be cut out from the system.—F. SODN.

Salt; Production of cooking —— *from rock salt.* L. W. Damman. Ger. Pat. 276,344, Sept. 20, 1913.

FINELY ground rock salt is introduced into a bolting mill in which it is moistened with a water spray. The treated salt contains 97% NaCl, is more crystalline than the original material, and does not cake on keeping.—A. S.

Alkaline [potassium] compounds [and cement] from alkali-bearing rocks [especially felspar] or weathering products; Method of producing soluble ——. P. Radmann, Godegard, Sweden. Eng. Pat. 12,136, May 16, 1914.

AN intimate mixture of alkali-bearing rock or weathering product and gypsum, to which limestone may be added, is heated below fusion point and the resulting mass treated, *e.g.*, by washing, to recover soluble alkali compounds. A suitable mixture contains 0·25—1 part by weight of gypsum to 1 part of felspar, to which up to 3 parts of limestone may be added; it should be pulverised to the "fineness of cement" and heated preferably to 1000°—1250° C. The residue, with or without limestone, may be burned to cement. —F. SODN.

Potash salts; Apparatus for treating, especially dissolving, salts such as crude ——. R. Fleischer. Ger. Pat. 276,070, Oct. 1, 1913.

IN a continuous apparatus for dissolving salts, the helical agitating blades are made with an arched cross-section, so that they act also as scoops for lifting the material and delivering it again into the liquid. The blades may be provided with transverse strengthening bars, which serve also to diminish the rate of flow of the material through the apparatus.—A. S.

Potassium and sodium salts from ashes of algae. C. Klingbiel. Ger. Pat. 277,109, Oct. 5, 1913.

THE solution obtained by lixiviating the ashes is treated with excess of phosphoric acid, and after the thiosulphates are decomposed, it is rendered neutral to methyl orange by addition of alkali, and treated in the usual way to separate potassium and sodium salts. The double sulphate of potassium and sodium is not formed, and the separation of the alkali salts by crystallisation can be carried further than has been possible hitherto, so that a final mother liquor of relatively small volume and rich in iodine is obtained, from which iodine can be recovered by treatment with chlorine.—A. S.

Nitrogen compounds; Electrochemical process for producing ——. J. W. Wood, Moulton, Iowa. U.S. Pat. 1,118,993, Dec. 1, 1914. Date of appl., Feb. 11, 1913.

SOIL containing alkali and/or alkaline-earth compounds is maintained in a moist state and subjected to an electric current, whilst air is being forced through the material, preferably from below. —F. SODN.

Bisulphite liquor [for paper making]; Apparatus for making ——, *using pyrites.* V. Drewsen, New York, U.S. Pat. 1,119,004, Dec. 1, 1914. Date of appl., Oct. 11, 1910.

WEAK sulphurous gases from a burner pass successively through a scrubber, having a continuous closed water circulation, and a gas cooler. A portion of the gases from the cooler then passes through a system of absorption towers, in which sulphur dioxide is absorbed by the circulation of an aqueous sulphurous liquor and finally of alkali liquor; at one point of this system sulphurous gases from the aqueous absorbent are recovered in concentrated form by operation of a heating device receiving heat from the hot gases. A system of tanks for making bisulphite, each having means for spraying the bisulphite or lime liquor therein, receives the concentrated sulphurous gases and another portion of the weak gases from the cooler, gases and liquor passing in opposite directions in the system.—F. SODN.

Hydrous alkali-metal silicate and method of producing it. E. A. Paterson, North Tonawanda, N.Y. U.S. Pat. 1,119,720, Dec. 1, 1914. Date of appl., June 20, 1914.

A DRY, amorphous alkali silicate containing a large proportion of silica, relatively little alkali, and less than 19% of combined water, is obtained in a spongy condition by subjecting a powdered alkali silicate, rich in silica, to a hydrating treatment, preferably by moistening with a solution of the same silicate and confining under low steam pressure, until sufficiently hydrated to be readily soluble in cold water.—F. SODN.

Colloidal solutions of metals; Manufacture of stable ——. B. Schwerin, Assignor to Elektro-Osmose A.-G. (Graf Schwerin-Ges.), Frankfort-on-the-Maine, Germany. U.S. Pat. 1,119,647, Dec. 1, 1914. Date of appl., April 18, 1914.

A METALLIC salt in solution is mixed with silicic acid and reduced, preferably with hydrazine hydrate.—F. SODN.

VIII.—GLASS; CERAMICS.

Lamps; Translucent marble for ——. Voege. Elektrotechn. Zeits. J. Gas Lighting, 1914, 128, 662.

MARBLE treated by H. W. Engel's process (this J., 1914, 87) was tested in regard to its power of diffusion and its transparency to visible, ultra-violet, and infra-red rays. Samples 3·5 mm. thick were compared with opaline and with ground glass. Photometric measurements showed that 67% of the illumination passed through the ground glass, 23% through the marble, and 19 and 14% through clear and dark opaline glass respectively. The marble screens were illuminated uniformly to the edges, and compared with opaline gave the impression of pure white. They also transmitted more of the red and blue, but absorbed green-yellow, thus giving a violet-red tint. Measurements of the radiating intensities from the vertical up to 90° showed that, in spite of its

great transparency, the marble was not inferior to opaline glass in dispersion. The treated marble was equally transparent to the visible and the ultra-violet rays, but absorbed the infra-red rays to an extent hitherto unknown.—W. C. H.

Fireclay goods, and their use in gas works. T. Holgate. J. Gas Lighting, 1914, **128**, 292—294, 363—364, 480—481, 536—537, 599—600, 661.

A REVIEW of the report of the Refractory Materials Committee of the Institution of Gas Engineers (see this J., 1914, 682). In regard to the effect of pressure on the melting point, results obtained with both English and American fireclays show that over a range from atmospheric up to 125 lb. per sq. in. additional pressure, the depression of the melting point is about 2·5° to 4° C. per lb. pressure. The depressions vary with different clays and do not seem to follow the normal melting points. Thus " a typical china clay of first-class quality," normally melting at 1770° C., melted at 1410° C. under a load of 112 lb. per sq. in., whereas another clay melted under corresponding conditions at 1750° C. and 1580° C. respectively, and its melting point was lowered by pressure less than that of any other mentioned. (See also Bleininger and Brown, this J., 1910, 1309; 1911, 1387.) From such data it seems possible to select material suitable for, say, gas-producers which would not stand the strain in retort settings. To ensure accuracy in tests of this kind, the importance of uniformity of treatment of the specimens and of the methods of heating is emphasised. Modern petrology has shown the important part played by hydrogen in the formation of minerals from a rock magma, and the author suggests that at the high temperatures at which fireclays are burned, it may also influence the nature of the finished product, and he illustrates the importance of the amount of combined water by reference to some recent work on fireclays of the Glenboig district. In the Report stress is laid on the necessity of keeping fuel ash, often highly ferruginous, from contact with brickwork. The injurious effects of iron oxides on firebrick increase in the order Fe_2O_3, Fe_3O_4, FeO, consequently reduction of ferric oxide by furnace gases must be prevented. Magnetic iron compounds can now be removed from clays on the large scale by the use of magnets (see this J., 1914, 257), but many iron compounds are only feebly magnetic. Pyrites can be removed if converted into oxide by roasting. The electro-osmosis process of purifying clay is also referred to (this J., 1914, 257). The magnetic properties of clay wares are due to magnetite and also to magnetic ferruginous silicates, and wares with speckled bodies, flashed surfaces, or black cores are always more magnetic than those free from such defects (see this J., 1913, 827). —W. C. H.

Grinding [of pottery materials] ; Fineness of——. F. Turner and A. Heath. Trans. Eng. Ceram. Soc., 1913—1914, **13**, 114—128.

POTTERY materials, whether pan or cylinder ground, generally pass a 130's lawn. Seventeen samples of commercial ground flint and stone were slipped with water, and sifted through 120's, 140's, 160's, 180's, 200's, and 250's lawns ; the total residue on the lawns ranged from 0·38 to 9·66%. Such variations may affect the properties of a body. Thus plasticity is reduced by coarse particles, and generally speaking contraction varies inversely, and porosity and crazing directly, as the size of the particles. Elutriated fractions of flint and stone, comprising particles up to 0·01 mm. in size, were further graded by being suspended in water and allowed to settle for several hours. It was found that the finest fraction melted at cone 2, whereas the coarsest was still

solid at cone 9. Similarly on firing, the finest contracted much more than the other fractions, and also " dunted."—W. C. H.

Leadless [pottery] glazes ; Notes on some——. J. A. Audley. Trans. Eng. Ceram. Soc., 1913—1914, **13**, 138—141.

THE following formulæ of Seger's were tried for covering fireclay with an opaque white glaze:—
$0·6 (K_2O, Na_2O), 0·4 CaO, 0·6 Al_2O_3, 5SiO_2, 1B_2O_3 $;
$0·3 K_2O, 0·7 CaO, 0·1 Al_2O_3, 2·5 SiO_2, 0·65 B_2O_3$;
$0·3 K_2O, 0·7 CaO, 0·1 Al_2O_3, 4 SiO_2, 1 B_2O_3$;
$0·3K_2O, 0·7CaO, 0·3Al_2O_3, 4SiO_2, 1B_2O_3$. The mixtures were fritted, ground, applied as a thick paste to unfired fireclay discs, and fired in a muffle. All gave a firmly adhering white enamel, the two last being very brilliant. Apparently the enamels are only produced within a limited range of temperature, for at an increased temperature transparent glazes were produced. When silica was substituted for the boric acid the materials were not vitrified completely. The enamels seemed equally satisfactory for either Stourbridge clay or local (Staffordshire) marl bodies, and most of the trial pieces could be dropped while red hot into cold water without the enamel crazing or cracking.—W. C. H.

The ternary system, $CaO–Al_2O_3–SiO_2$. Rankin and Wright. See IX.

IX.—BUILDING MATERIALS.

[Portland cement clinker.] *The ternary system, $CaO–Al_2O_3–SiO_2$.* G. A. Rankin and F. E. Wright. Amer. J. Sci., 1915, **39**, 1—79.

FOLLOWING previous investigations in the U.S. Geophysical Laboratory (see this J., 1907, 95 ; 1909, 1124 ; 1911, 543), the authors studied all the compounds, both binary and ternary, which are found in dry fused mixtures of CaO, Al_2O_3, and SiO_2, with regard to melting points, dissociation temperatures, invariant points, location of eutectics, boundary curves of monovariant systems, and fields of stability of divariant systems. The data obtained are used to discuss the nature and constitution of Portland cement clinker and the formation of certain natural minerals from the magma. Of the three components, the respective melting-points of pure lime and alumina (artificial corundum) are given as 2570° and 2050° C. (Kanolt) ; while the melting-point of silica is said to be variable according to the progress of its inversion, viz., α quartz—β quartz—β, tridymite—β crystobalite and α tridymite—β, tridymite—β, tridymite —α crystobalite—β crystobalite. Metastable quartz melts at about 1470° C. and crystobalite at 1625° or higher. In the binary system $CaO–SiO_2$, four distinct compounds exist, viz., CaO, SiO_2 ; $3CaO, 2SiO_2$; $2CaO, SiO_2$, and $3CaO, SiO_2$, most of which appear in more than one crystalline form. CaO, SiO_2 in the β-CaO form is the mineral wollastonite, and, in the α-CaO form, pseudowollastonite, which has not been found in nature but only in artificial slags. In the binary system, $Al_2O_3–SiO_2$, only one compound, sillimanite, appears ; it forms eutectics both with Al_2O_3 and SiO_2. The $CaO–Al_2O_3$ system contains four distinct compounds : $3CaO, Al_2O_3$; $5CaO, 3Al_2O_3$; CaO, Al_2O_3, and $3CaO, 5Al_2O_3$, most of which are dimorphous. Investigation of the ternary system, $CaO–Al_2O_3–SiO_2$, which necessitated 7000 experiments, with subsequent optical examination, showed that there are three new crystalline phases not found in the binary series ; that there are 14 fields of stability, 30 boundary curves, and 21 quintuple points. Two of the new compounds, $CaO, Al_2O_3, 2SiO_2$ (artificial anorthite)

and $2CaO,Al_2O_3,SiO_2$, are stable in contact with the fused material ; the other, $3CaO,Al_2O_3,SiO_2$, is not. The fields of stability for 14 compounds, including the original components, are described ; and also the boundary curves and quintuple points, with concentration-temperature models and diagrams, and a final table of all the results. From these data and the theory of crystallisation it is possible to predict which substances will separate out from any slowly cooling solution containing only CaO,Al_2O_3, and SiO_2, the order in which they separate, and the corresponding temperatures. Although the diagram exhibiting the final products of crystallisation presupposes the continuous attainment of equilibrium, yet it is possible to predict with considerable certainty the final product even when the reaction has not proceeded to completion. This occurs with Portland cement clinker, which would be essentially a mixture of $3CaO,SiO_2$; $2CaO,SiO_2$; $3CaO,Al_2O_3$, with some $5CaO,Al_2O_3$ and possibly free CaO ; a conclusion which has been confirmed by the work of the U.S. Bureau of Standards on commercial clinkers (see Bates, this J., 1914, 81).—H. H. S.

Cement. Board of Trade Bulletin No. 71.

THE value of cement exported from Germany, Austria-Hungary, and the United Kingdom, respectively, to all destinations was as follows :— From Germany (1912) : Portland cement, Roman cement, and hydraulic cements (tufa, trass, puzzolana, and puzzolana-sand, etc.), £1,723,900. From Austria-Hungary (1913) : Portland cement, Roman cement, and other artificial cement, £215,900. From the United Kingdom (1913) : Cement for building and engineering purposes, £1,273,100. In 1912 the value of Germany's exports of cement to the United Kingdom were valued at only £28,600, while no cement was exported from Austria-Hungary to this country.

The principal destinations to which German cement was exported, and the value of such exports in each case, were as follows :—Brazil, £281,300 ; Netherlands, £249,700 ; Chile, £142,300 ; Australia, £133,800 ; Russia, £111,700 ; France, £56,800 ; Dutch East Indies, £55,700 ; Turkey, £50,900 ; Philippines, £40,300 ; Uruguay, £29,800 ; and Belgium, £28,900 ; while a fair trade was done with the United States, Portuguese East Africa, and India. Austrian exports of cement in 1913 included : Bulgaria, £16,600 ; Russia, £18,950 ; Turkey, £13,425 ; Tripoli, £11,920 ; Argentina, £18,400 ; and Brazil, £12,800.

About one-half of our aggregate exports of cement goes to India, Ceylon, British Africa, and Australia, while one-third goes to Argentina and Brazil. The balance is spread over a number of small markets, of which the more important in 1913 were Spain, Egypt, Chile, and Uruguay.

Producing soluble alkali compounds [and cement] from alkali-bearing rocks. Eng. Pat. 12,136. *See* VII.

X.—METALS ; METALLURGY, INCLUDING ELECTRO-METALLURGY.

Steel ; Microscopic examination of ——. B. Strauss. Verein deutscher Chemiker, June 6, 1914. Z. angew. Chem., 1914, 27, 633—645.

A RESUMÉ of our knowledge of the micro-structure of carbon-, nickel-, and chromium-steels is given, together with photomicrographs, some in natural colours. Hitherto only the pearlitic chrome-nickel-steels have been used industrially, but recent work in the research laboratory of Krupp's has resulted in the production of high-percentage

chrome-nickel-steels of martensitic and austenitic structure. These have good mechanical properties and are very resistant to corrosion and to the action of acids. Instances are cited where microscopic examination has revealed the cause of failure of boiler tubes, axles, and tyres of railway wagon wheels. In electrically welded steel joints up to 0·12 % N has been detected, and in joints made with the oxy-acetylene flame up to 0·02 % N. When ammonia or nitrogen is led through molten iron, the metal only fixes 0·03—0·04 % N, but by the action of ammonia on solid iron, up to 11·1 % N (corresponding to Fe_4N_2) may be combined : fixation of nitrogen commences at about 300° C., and is most vigorous at 600°—800° C., diminishing again above 800 C. The micro-structure of nitrogenised iron is described and illustrated, and, in agreement with Le Chatelier (Rev. Mét., 1905, 506), the lines considered by Hanaman (Dissertation, Berlin, 1913, 30) to be due to needles of iron nitride, are regarded as analogous to Neumann lines and due to deformation, which is facilitated by the brittleness conferred on the ferrite grains by their nitrogen content. Bars of mild steel, 12·5 mm. diam., containing C 0·07, Si 0·05, Mn 0·30, P 0·021, S 0·014, Cu 0·06, and N 0·004 %, were nitrogenised to different degrees, then the outermost layer was removed, and the mechanical properties of the bars (12 mm. diam.) determined. The results were :—

Heated at 700° C. in :		N.	Elastic limit.	Tensile strength.	Elonga-tion.	Con-traction.
		%	kilos. per sq. mm.	kilos. per sq. mm.	%	%
Ammonia,	24 hours	0·10	32·7	41·6	24·2	75
,,	48 ,,	0·11	32·7	41·1	21·8	75
,,	72 ,,	0·16	35·0	42·8	22·5	71
,,	96 ,,	0·22	34·0	44·9	21·8	66
Hydrogen,	48 ,,	0·004	30·1	35·4	31·8	81
Nitrogen,	48 ,,	0·004	28·4	34·7	31·5	81

The magnetic properties of iron are deteriorated by nitrogen : the permeability is diminished and the hysteresis and coercive force increased ; in the case of a mild steel containing about 4 % Si, nitrogen caused a considerable increase in the hysteresis, without increasing the coercive force. If iron containing silicon or chromium be nitrogenised at about 800° C., nitrides of these elements are formed, which, unlike iron nitride, are very stable.—A. S.

Steel ; Influence of titanium on the properties of ——. F. A. J. Fitzgerald. Met. and Chem. Eng., 1915, 13, 28—29.

IN the production of 9000 tons of steel rails, from 155 heats made under uniform conditions except as regards the presence or absence of added titanium, the proportion of heats yielding rails within the specification limits in regard to segregation was 36 % when no titanium was used, and 43, 84, and 100%, respectively, when the steel contained 0·053, 0·077, and 0·10 % Ti (see also Comstock, this J., 1915, 55—57).—W. E. F. P.

Iron ; The corrosion of —— *and its application to determine the relative strengths of acids.* J. A. N. Friend and C. W. Marshall. Chem. Soc. Trans., 1914, 105, 2776—2782.

EXPERIMENTS were made to determine the relationship existing between the minimum quantity of alkali required to inhibit the corrosive action of different salts, and the relative strengths of the acids and bases constituting the salts. Sodium and potassium carbonates and borax were used as inhibitors, and added in varying

quantities to a definite amount of a sodium salt, viz., the chloride, iodide, bromide, sulphate, nitrate, fluoride, acetate, sulphite; the results showed that when the salts are arranged in descending order of inhibiting carbonate concentrations, not only are they in the order of decreasing electrical conductivity of their acids, but the relative quantities of carbonate solution bear a general relationship to the values found for the strengths of the acids by electrical conductivity and hydrolysis methods. Experiments were also made with some of the above salts to determine the concentration at which auto-inhibition just begins, but the results were not comparable with those obtained by the addition of inhibitors. The curves obtained by plotting the quantities of sodium carbonate required to inhibit corrosion in the presence of varying quantities of sodium salts, show a distinct resemblance to the specific conductivity curves of the free acids corresponding to the salts, obtained from the data published by Kohlrausch.—B. N.

Silver; The removal of sulphur from ———. C. C. Bissett. Chem. Soc. Trans., 1914, **105**, 2829—2836.

THE addition of copper to molten silver is of little use for the removal of sulphur, but by adding a considerable excess of iron above the amount required to saturate the sulphur, the latter is removed as ferrous sulphide. The sulphur can also be slowly removed by blowing dry air through the molten silver at about 1000° C.—B. N.

Output of certain minerals and metals in the world. [Cd. 7732.]

THE Colonial and Foreign section (Part IV.) of the Mines and Quarries Report for the year 1912 contains a table showing the output of certain minerals and metals (contained in or obtained from ore raised) in the British Empire and in foreign countries during 1912, which may be summarised as follows :—
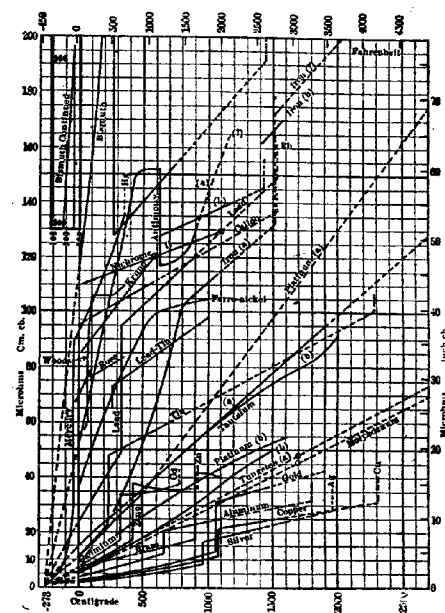
for each material, the source, etc., of the information given. The curves relating to various

Iron: curve (a) from data given in Landolt and Börnstein's Tables and by Somerville (Phys. Rev., **31**, 268); (b) from von Baur's data. *Antimony*: (a) from data of Northrup (J. Franklin Inst., 1913, 153), and (b) from figures of Bornemann and von Rauschenplat (Tables Annuelles de Constantes, **2**, 258). *Platinum*: (a) from data in Landolt and Börnstein's Tables. *Tungsten*: (a) from Fink's figures (see this J., 1910, 825). *Tantalum*: (a) from Siemens' figures. The (b) curves for *platinum*, *tungsten*, and *tantalum* are from Pirani's data (Tables Annuelles de Constantes, **1**, 227).

		United Kingdom.	British Colonies, Dependencies, and Possessions.	Foreign Countries.	Total for the World.
Coal	Metric tons	264,595,395	49,886,732	935,413,858	1,249,895,985
Copper	”	296	88,998	942,189	1,031,483
Fine gold	Kilos.	41	435,850	276,592	712,483
Iron	Metric tons	4,523,074	1,150,493	66,737,909	72,411,481
Lead	”	19,461	242,785	872,998	1,135,244
Petroleum	”	—	1,102,342	46,084,121	47,186,463
Salt	”	2,156,307	1,708,709	14,105,237	17,970,253
Fine silver	Kilos.	3,825	1,552,804	5,626,889	7,183,518
Tin	Metric tons	5,338	60,798	59,582	125,718
Zinc	”	6,159	203,026	808,564	1,017,749

The quantities of metals included are those which are considered obtainable from the ores raised in the countries in question, and must not necessarily be taken as a measure of the metallurgical industries of those countries. The total value of the estimated output shown in the table may be taken as representing about £1,047,000,000.

Electric resistances [of metals and alloys] at high temperatures; Comparisons of ———. C. Hering. Met. and Chem. Eng., 1915, **13**, 23—28.

EXISTING data, conveniently grouped, are correlated and represented by 5 uniform sets of curves; and notes are appended indicating,

metals and alloys are shown in the accompanying chart.—W. E. F. P.

Mercury imports and exports; British ———. Chem and Drug., Jan. 30, 1915.

	Imports. Bottles.	Exports. Bottles.
1906	38,823	27,712
1908	43,605	22,348
1910	44,595	24,748
1911	46,547	31,438
1912	47,261	32,240
1913	45,348	26,815
1914	37,568	22,975

NOTE.—A bottle of mercury is 75 lb.

D 3

Separation of tungsten from molybdenum. Marbaker.
            See XXIII.

*Iron ; Electrolytic production of malleable or
    forgeable ——.* E. F. K. Harbeck. Partille,
    Sweden. Eng. Pat. 1437, Jan. 19, 1914.

MALLEABLE iron of any desired thickness is
obtained electrolytically by the use of a solution
of ferrous silicofluoride or fluoride, free from other
metals, as electrolyte.—B. N.

Ferrophosphorus ; Manufacture of——. D. I.
    Miller, Birmingham, Ala. U.S. Pat. 1,115,471,
    Oct. 27, 1914. Date of appl., May 6, 1914.

SUITABLE basic material (limestone) is mixed with
natural phosphate rock and iron ore in the correct
proportions to yield the proper ratio of acids to
bases in the slag, and to liberate the required
percentage of phosphorus, and the mixture is
smelted with coke in a blast furnace. The process
is applicable to natural phosphate rock too rich
in silica to be used economically for the manu-
facture of fertilisers.—T. ST.

*Solutions [e.g. cyanide slimes]; Apparatus for
    treating solid-bearing ——.* L. C. Trent. Los
    Angeles, Cal., U.S.A. Eng. Pat. 24,413, Oct. 28,
    1913.

AN apparatus for settling, decanting, and washing
cyanide slimes and the like. The material is
delivered from a launder into a short, depending,
perforated cylinder situated centrally at the
top of the vat. The cylinder is closed at its
lower end by a conical deflector which distributes
the material gently into the body of liquid in the
vat. Near the bottom of the vat is a ring-pipe
provided with holes in its under surface, and
below this is a centrifugal agitator, the hollow
radial arms of which are provided with nozzles.
A pump withdraws fluid through the ring-pipe,
and returns it through the nozzles of the agitator
which thus revolves, and, by means of scrapers,
forces the thickened mud towards outlets in the
bottom of the vat. A by-pass between the with-
drawal and return pipes, controlled by a valve,
serves to regulate the flow of material. The vat
is provided with try-cocks at different levels for
testing the quality of the liquid.—T. ST.

[Ore] separators ; Magnetic ——. A. F. Jobke,
    Cleveland, Ohio, U.S.A. Eng. Pat. 26,364,
    Nov. 17, 1913.

THE field of the separator has a working gap
divided into zones of different strengths, which
can be varied by varying the "reluctances" of the
circuits corresponding to the several zones, without
varying the length of the gaps which form the
zones. For instance, the reluctances between
adjacent members forming the zones may be
varied, or removable magnetic elements may be
used. The variation may be provided in the
members of one or both sides of the working gap
and one or both opposing pole elements may be
formed in sections spaced apart, opposing sections
forming a zone of the gap, and the spacing pro-
viding the circuit reluctance. Both poles may be
built up of a member of minimum reluctance
and a section formed of laminations of alternately
high and low permeability for increasing the
reluctance of the section. A number of fields
may be formed by primary and secondary mag-
netic structures, to cause each field to act as a
working gap divided into zones of different
strengths, adjacent zones being formed by spacing
adjacent members of both primary and secondary
structures to provide reluctance between members
of similar polarity, the reluctance of the field

circuits being variable by varying the reluctances
of the secondary magnet members.—B. N.

Ores ; Treatment of ——. O. C. Rudolph, London.
            Eng. Pat. 29,156, Dec. 17, 1913.

COMPLEX sulphide ores containing Cu, Pb, Zn,
and Fe, with Ag and Au, are smelted, with the
addition of fluxes if necessary, in an electric furnace
to form a matte, which is then blown in a con-
verter. The volatile matter driven off in both
stages is passed through a wet condenser, where an
acid solution of zinc sulphite and sulphate, with
lead sulphite and sulphate in suspension, is formed.
When the solution becomes sufficiently rich in
zinc salts, it is freed from the lead precipitate and
electrolysed, using perforated anodes. Two forms
of condenser are described, both similar in principle,
and each formed of a series of compartments:
the first compartment is designed to retain solid
matter suspended in the gases ; the second is
composed of fire- and acid-proof brick chequer-
work, down which water is caused to trickle;
the remaining compartments are provided with
superposed rows of wooden baffle-rods, down
which water trickles. The uncondensed and
unabsorbed gases are finally drawn off to a
chimney.—T. ST.

*Sulphide ores and other metallic sulphides ; Process
    of treating ——.* K. Birkeland, Christiania,
    Norway. U.S. Pat. 1,121,606, Dec. 22, 1914.
    Date of appl., Jan. 23, 1913.

THE ores are treated with steam superheated by a
flaming arc, the hydrogen produced being separated
from the issuing gases, and passed in again with
fresh quantities of steam.—O. E. M.

Zinc-furnace. O. E. Ruhoff, Madison, Wis. U.S.
    Pat. 1,121,874, Dec. 22, 1914. Date of appl.,
    March 26, 1914.

AN electric resistance furnace is provided with a
considerable number of electrodes, distributed so
as to ensure uniform heating of the charge, which
itself constitutes the resistance. The zinc is con-
densed in a relatively large number of clay con-
densers, supplementary condensers with coal
barriers being provided for blue powder.—O. E. M.

Distillation furnace for zinc and the like. H.
    Hantelmann. Ger. Pat. 276,292, March 28,
    1913.

THE furnace is mounted on horizontal hollow
trunnions and contains only a single muffle, which
is heated by the Bone system of surface com-
bustion. The supply of gas and air is introduced
through the trunnions, and can be cut off
merely by rotating the furnace, which, normally,
is held stationary by an easily movable spring
device. Two such furnaces may be connected
independently with a common supply of gas and
air.—A. S.

Copper ; Hardening and welding ——. C. Bittner,
    Stafford, Kans. U.S. Pat. 1,122,062, Dec. 22,
    1914. Date of appl., June 6, 1914.

COPPER is heated to a cherry red, and successive
portions of its surface are treated with sodium
"hyposulphite" and acetic acid, with or without
alum. The treatment may be repeated at a lower
temperature.—O. E. M.

Aluminium alloy ; Hard ——. W. de l'Or. Ger.
    Pat. 277,121, May 28, 1913. Addition to Ger.
    Pat. 265,924.

THE quantity of lead in the alloy described in the
chief patent (this J., 1913, 1160) is diminished

about one-half. The portion of lead omitted may be replaced by a somewhat larger quantity of tin.
—A. S.

Nickel; Process for improving the mechanical and chemical resistance of ——. Siemens und Halske A.-G. Ger. Pat. 277,242, March 4, 1913.

NICKEL is alloyed with tantalum. An alloy with 30% Ta is non-magnetic, can be easily rolled, forged, and drawn, and is equal to steel in elasticity and tensile strength. It is not attacked by boiling *aqua regia* or other acids, and is not oxidised when heated in the air, but may become brittle when very strongly heated.—A. S.

Iron and steel; Art of making ——. W. J. Mellersh-Jackson, London. From Billings Process Co., Birmingham, Ala. U.S.A. Eng. Pat. 21,048, Sept. 17, 1913.

SEE U.S. Pat. 1,073,587 of 1913; this J., 1913, 1017.

XI.—ELECTRO-CHEMISTRY.

Silver voltameter; The inclusion of electrolyte by the deposit in the ——. T. W. Richards and F. O. Anderegg. J. Amer. Chem. Soc., 1915, 37, 7—23.

THE amount of electrolyte included in the crystallised silver deposited in a silver voltameter varied with increasing surface and roughness of the cathode from 0·004 to 0·035% of the weight of the silver. Very pure silver remained after a brief ignition of the deposit at incipient redness, under which treatment the metal was not sensibly volatile. The experiments of the English, American, and German national bureaus upon this point and the results of other investigators in the field are adversely criticised. The correction is important in determinations of the values of the Farad, the standard Weston cell, electrochemical equivalents, and ratios of atomic weights. (See also this J., 1915, 91.)—J. R.

Electrolysis of solutions of the rare earths. Dennis and Lemon. *See* VII.

Electric resistivities [of metals and alloys] at high temperatures. Hering. *See* X.

PATENTS.

Electrical conductor. T. B. Allen and L. B. Coulter, Assignors to The Carborundum Co., Niagara Falls, N.Y. U.S. Pat. 1,121,601, Dec. 22, 1914. Date of appl., Sept. 24, 1913.

THE conductor consists of a porous base of silicon carbide impregnated with graphite, in a fine state of subdivision, equal to that of colloidal graphite when freed from moisture. It is characterised by practically uniform conductivity and high resistance to electrical discharge, and is given a coating impervious to oxygen at high temperatures.
—B. N.

Electrochemical process for producing nitrogen compounds. U.S. Pat. 1,118,993. *See* VII.

XII.—FATS; OILS; WAXES.

Castor beans; The esterase and lipase of ——. *(Studies on enzyme action. XII.)* K. G. Falk and K. Suguira. J. Amer. Chem. Soc., 1915, 37, 217—230.

THE residue remaining after extracting the ground kernels of cold-pressed castor-beans with ether, gave results identical with those previously described for a somewhat different preparation when extracted with water and different saline solutions (see J. Amer. Chem. Soc., 1913, 35, 1904): 70% of the material (esterase) active

towards ethyl butyrate and 33% of that (lipase) active towards triacetin could be extracted with water. The activity of the preparation was unaffected by drying *in vacuo* over calcium chloride or phosphorus pentoxide; the considerable decrease in activity noticed on heating to 100°—110° C. is attributed to chemical change. An esterase preparation, probably identical with glycerophosphatase, was isolated by extraction with water, and a lipase preparation by extraction with 1·5-N sodium chloride solution. The relative proportions of the different forms of nitrogen in these two preparations and the original castor bean preparation were essentially the same, and the preparations appear to possess a protein nature.
—J. R.

Oils from less known seeds and fruits. E. R. Bolton and E. M. Jesson. Analyst, 1915, 40, 3—9.

RECENT introduction of machinery for separating the kernels from very hard nuts has enabled several little-known oils to be put upon the market. (1) *Balanites Maughamii, Sprague* (Portuguese E. Africa) yielded an olive-green pulp oil (4·4%) with a pronounced odour of butyric acid, and a valuable kernel oil (45·5%), which as yet cannot be obtained as a commercial product owing to the difficulty of separating the sticky pulp. (2) The pale yellow, semi-solid oil of *Calophyllum tomentosum, Wight.* (India) has an unpleasant odour. The kernel contains 70·3% and the whole fruit 50% of oil. (3) The kernels of *Calophyllum inophyllum, L.* (dhomba nuts) yielded 70·1% of a brownish-green oil. Although stated by Lewkowitsch to be poisonous, this is used as an edible oil by the natives of India. (4) *Melia azadirachta, L.* (" beni seeds," S. America), yielded a clear oil (" neem " or " margosa oil ") containing much unsaponifiable matter, and having an odour of garlic. The kernel contained 43·6% and the whole fruit 14·8%. (5) *Fevillea cordifolia, L.* (Tropical America and W. Indies) yielded a solid fat (57·6% of the kernels) with unpleasant odour and bitter taste. Its refractive index was exceptionally high and it had good drying properties. (6) The seeds of *Telfairia pedata, Hook* (jiconga nuts: Tropical Africa), yielded 60·9% of a pale yellow oil with little odour but bitter taste. Oil expressed from the whole fruit (35·9%) is said to contain toxic substances (Bontoux). (7) The seeds of *Canarium luzonicum, Miquel* (" pili nuts," Philippine Islands) contained 72·2% of a semi-solid fat with pleasant odour and taste. The kernels, which are used by the natives as substitutes for sweet almonds, are rich in proteins. (8) A semi-solid oil of pale yellow tint (macassar oil) was separated from the kernels of *Schleichera trijuga, Willd.* (India), known locally as nitas beans. Its high Reichert-Meissl value would render its detection in butter difficult, but for a peculiar colour reaction on saponification. The kernels contained 71·9% of oil. (9) *Sterculia fœtida, L.* (" Java olives "):—The kernels (kaloem-pang beans or beligho seeds) yielded 52% of a viscous oil, which solidified when heated to 250° C., and gave a pronounced reaction in Halphen's cotton-seed-oil test. It would be suitable for salad oil. The pulp contained 6·9% of oil. (10) *Anacardium occidentale L.* (cashew nuts; S. America, W. Indies) yielded 44·8% of a pale yellow oil, which is not often separated owing to the high price of the kernels. (11) *Buchanonia latifolia, Roxb.* (" Peru palm kernels," India and Burma) contains 61% of a pale oil (chironjii oil) of pleasant odour and taste. (12) A soft browish-green fat may be separated both from the seed (7·1%) and the fibrous shell of *Œnocarpus distichus, Mart.* (S. America). (13) Fruit termed *Marquaqua nuts* (Portuguese E. Africa) of an unidentified plant yielded 20% of a dark golden-yellow, somewhat viscous oil.

	1	2	3	4	5	6	7	8	9			10	11	12	13
	Pulp oil.	Kern oil.								Pulp oil.	Kernel oil.				
M. pt., °C.	—	—			34		29							36	
Solidif. pt., °C.	—	—1°	25	17	35 (turbidity pt.)		6	14	20	—6			18		4
Saponif. value	—	191.5	170.5	190.5	185.6	192.9	193.6	197.0	227.0	—	193.8	193.7	198.7	209.2	189.3
Refractometer (Zeiss. 40°C)	51.8°	57°	72.7	72.3	54.1	77.1	54.5	48.6	50.6	63.2	59.8	54.4	49.3	49.0	49.7
Iodine value (Wijs)	77.5	100.6	93.7	88.5	72.9	52.4	90.4	57.1	54.5	66.3	75.8	79.5	54.9	55.0	70.1
Free fatty acids % (as oleic)	79.0	1.22	3.46	26.2	3.15	0.28	0.31	1.44	7.93	—	1.0	0.8	4.45	65.9	15.3
Unsapon. matter %		0.88	4.0	1.2	7.7									2.15	1.26
Reichert-Meissl value					8.27				16.0						
Polenske value					0.25				0.27						
Kirschner value					4.96				14.5						

—C. A. M.

Action of fused potassium hydroxide on dihydroxystearic and dihydroxybehenic acids. Le Sueur and Withers. See XX.

Use of hydrogenised fish oil in the manufacture of margarine. Klimont and Mayer. See XIXA.

Feeding stuffs (oil cake). Board of Trade Bulletin. See XIXA.

PATENTS.

Fats and fatty emulsions and the like; Process for cooling hot or molten ——. Naamlooze Vennootschap Ant. Jurgens' Vereenigde Fabrieken, Oes, Holland. Eng. Pat. 10,863, May 2, 1914. Under Int. Conv., Feb. 26, 1914.

THE fat, etc., at a temperature a little above its m. pt., is taken up in an uniform layer on the periphery of a heated rotating cylinder, and is thence conveyed to the periphery of an adjacent cooling cylinder, which may rotate in the same direction but at a lower speed than the feeding cylinder.—C. A. M.

Unsaturated compounds [oils]; Process and apparatus for hydrogenating ——. H. K. Moore, Berlin, N.H. U.S. Pat. 1,121,860, Dec. 22, 1914. Date of appl., Feb. 26, 1914.

SEPARATE streams or an intimate mixture of oil and hydrogen are passed continuously through a finely-divided catalytic agent, which may be contained within a diaphragm porous to the oil and hydrogen, but impervious to the catalyst.—C. A. M.

Soaps; Process for improving the washing properties of neutral —— and at the same time increasing their keeping properties by admixture of hydrocarbons. C. Pleines, Gemlinde Zeist, Holland. Eng. Pat. 29,122, Dec. 17, 1913.

SEE Fr. Pat. 466,331 of 1913; this J., 1914, 603. Reference is directed, in pursuance of Sect. 7, Sub-sect. 4, of the Patents and Designs Act, 1907, to Eng. Pats. 16,329 of 1887, 13,700 of 1889, 13,853 of 1894, 16,406 of 1905, 7380 of 1906, 8982 of 1909, and 27,959 of 1912.

XIII.—PAINTS; PIGMENTS; VARNISHES; RESINS.

Painters' colours and materials (including varnish). Board of Trade Bulletin.

THE aggregate value of painters' colours and materials (including varnish) exported to all destinations from Germany, Austria-Hungary, and the United Kingdom respectively in a recent year reached the following amounts: From Germany (1912), £3,162,000; from Austria-Hungary (1913), £219,500; from United Kingdom (1913), £3,286,300. While the United Kingdom is quite an important market for these products for both Germany and Austria-Hungary, the United Kingdom sends little to them in return.

The principal descriptions of paints, etc., exported by Germany and Austria-Hungary in a recent year, so far as the particulars are available, were as follows:—

Article.	Exported from Germany (1912).		Exported from Austria-Hungary (1913).	
	To all Destinations.	To Principal Neutral Markets.	To all Destinations.	To Principal Neutral Markets.
	£	£	£	£
Zinc white	448,500	338,000	} 142,400	44,600
Zinc grey	113,000	38,000		
White lead	256,500	216,000	700	370
Ultramarine; lakes, etc., of ultramarine	100,000	61,000	15,000	9,340
Bronze metal colours	316,000	273,000	2,900	800
Natural and artificial iron oxide (including yellow ochre), roasted, etc.	72,500	30,000	} 15,809	3,650
Umber, sienna earth, and other unspecified mineral colours	153,500	92,500		
Lithopone; Griffith's white	166,000	115,000	6,400	4,500
Colours for colour printing on paper prepared from lamp-black or Frankfurt black; printing ink and Frankfurt black	155,500	65,000	5,600 (prepared blacks).	4,915
Barytes	208,000	152,000		
Zinc powder	102,000	53,000	12,300 (unspecified colours.)	7,150
Pure and mixed blues; lakes, etc., of Prussian blue, chrome green, zinc green	115,000	75,000	6,100 (Colours in cakes, small bags, pastes, tubes, bladders, flakes, glasses, shells, and boxes.)	5,170
Chrome colours	102,000	51,000		
Red lead	196,500	142,500		
Copper colours (except Schweinfurt green) and other unspecified pigments and lakes, dry or paste	151,000	103,500		
Prepared colours not specified (ground with oil, oil varnish, glycerine, etc.); unprepared colours in small bags	259,000	166,500		
Varnishes and lacquers	247,000	140,000	12,300	9,665
Total	3,162,000	2,112,000	219,500	90,160

The particulars as to British exports to the more important Colonial and neutral markets in 1913 were as follows :—

Article Exported.	To all Destinations	To Principal Colonial and Neutral Markets
	£	£
Barytes	20,100	7,500
White lead	504,700	127,200
Zinc oxide	54,900	21,700
Unenumerated (including varnish)	2,706,700	1,888,500
Total .... £	3,286,400	2,044,900

The following detailed particulars show for a recent year the value of various descriptions of painters' colours and materials (including varnish) exported from Germany and Austria-Hungary, respectively, to the principal markets :—

(a) *Exports from Germany* (1912). *Barytes :*—United Kingdom, £98,000 ; Canada, £3,000 ; France, £4,000 ; Russia, £26,000 ; Argentina, £4,000 ; United States, £17,000. *Zinc White :*—United Kingdom, £138,000 ; Canada, £15,000 ; Norway, £22,000 ; Sweden, £33,000 ; Denmark, £18,000 ; France, £25,000 ; Russia, £19,000 ; United States, £51,000. *Zinc Grey :*—United Kingdom, £32,000 ; Norway, £2,000 ; Sweden, £4,000. *Red Lead :*—United Kingdom, £75,000 ; Canada, £5,000 ; British India, £14,000 ; Sweden, £7,000 ; Denmark, £6,000 ; France, £4,000 ; Portugal, £4,000 ; Italy, £2,000 ; Russia, £7,000 ; Dutch East Indies, £2,500 ; Brazil, £6,000 ; Argentina, £7,000 ; United States, £3,000. *White Lead :*—United Kingdom, £152,000 ; British India, £2,000 ; Sweden, £8,000 ; Denmark, £10,000 ; France, £5,000 ; Spain, £4,000 ; Portugal, £7,000 ; Russia, £6,000 ; Turkey, £5,000 ; Argentina, £17,000. *Pure and Mixed Blues, Lakes, etc., of Prussian Blue, Chrome Green, Zinc Green :*—United Kingdom, £26,000 ; British India, £5,000 ; Sweden, £4,000 ; Denmark, £3,000 ; Italy, £8,000 ; Russia, £11,000 ; China, £2,000 ; Japan, £4,000 ; Brazil, £3,000 ; United States, £8,000 ; Mexico, £1,000. *Ultramarine, Lakes, etc., of Ultramarine :*—United Kingdom, £33,000 ; Spain, £14,000 ; Italy, £3,500 ; Japan, £5,500 ; United States, £5,000. *Zinc Powder :*—United Kingdom, £17,000 ; British South Africa, £3,000 ; Denmark, £2,000 ; China, £4,000 ; United States, £25,000 ; Mexico, £2,000. *Lithopone :*—United Kingdom, £47,000 ; Canada, £5,000 ; Denmark, £3,000 ; Sweden, £4,000 ; France, £43,000 ; Italy, £4,000 ; United States, £9,000. *Natural and Artificial Iron Oxide (including Yellow Ochre), roasted, etc. :*—United Kingdom, £4,000 ; Australia, £2,000 ; Sweden, £2,000 ; Denmark, £2,000 ; France, £6,000 ; Italy, £1,000 ; Russia, £5,000 ; Brazil, £2,000 ; Argentina, £4,000 ; United States, £2,000. *Umber, Sienna Earth, and other Unspecified Mineral Colours :*—United Kingdom, £16,000 ; Australia, £2,000 ; British India, £3,000 ; Sweden, £7,000 ; Denmark, £5,500 ; France, £8,000 ; Spain, £3,500 ; Italy, £7,000 ; Russia, £11,000 ; Egypt, £4,000 ; Brazil, £6,000 ; Argentina, £3,500 ; United States, £12,000. *Bronze (Metal) Colours :*—United Kingdom, £38,000 ; Canada, £3,000 ; British India, £2,000 ; France, £45,000 ; Spain, £5,000 ; Italy, £9,000 ; Russia, £40,000 ; China, £3,000 ; Japan, £3,000 ; Brazil, £3,000 ; Argentina, £2,000 ; United States, £118,000. *Chrome Colours :*—United Kingdom, £23,000 ; Sweden, £5,000 ; Denmark, £3,000 ; France, £5,000 ; Italy, £5,000 ; Russia, £4,000 ; Japan, £2,000 ; United States, £4,000. *Copper Colours (except Schweinfurt Green) and other Unspecified Pigments and Lakes, dry or paste :*—United Kingdom,

£39,000 ; British India, £2,000 ; Sweden, £7,000 ; France, £3,000 ; Italy, £10,000 ; Russia, £5,000 ; China, £1,500 ; Japan, £7,000 ; United States, £24,000. *Colours for Colour-Printing on Paper, prepared from Lamp-Black or Frankfurt Black, Printing Ink and Frankfurt Black :*—United Kingdom, £8,000 ; British India, £2,000 ; Norway, £5,000 ; Sweden, £6,000 ; Denmark, £6,000 ; France, £8,000 ; Spain, £7,000 ; Italy, £6,000 ; Russia, £5,000 ; Brazil, £4,000 ; Argentina, £8,000. *Prepared Colours, not specified (ground with Oil, Oil Varnish, Glycerine, etc.) ; Unprepared Colours in small bags :*—United Kingdom, £17,000 ; Australia, £3,000 ; British India, £3,000 ; British West Africa, £3,500 ; Norway, £5,000 ; Sweden, £10,000 ; Denmark, £10,000 ; France, £8,000 ; Spain, £9,000 ; Italy, £19,000 ; Roumania, £3,000 ; Russia, £8,000 ; Egypt, £1,000 ; China, £5,000 ; Japan, £6,000 ; Brazil, £15,000 ; Uruguay, £3,000 ; Argentina, £10,000 ; Chile, £5,000 ; United States, £13,000 ; Mexico, £3,000. *Lac Varnish, Lacquers (not containing spirit) ; Asphalt, Varnish, Coach-maker's Varnish, Japan Varnish :*—United Kingdom, £28,000 ; Norway, £8,000 ; Sweden, £11,000 ; Denmark, £20,000 ; France, £9,000 ; Spain, £5,000 ; Italy, £22,000 ; Russia, £7,000 ; Turkey, £3,000 ; China, £3,000 ; Brazil, £4,000 ; Argentina, £6,000 ; Chile, £2,000 ; United States, £12,000.

(b) *Principal Exports from Austria-Hungary* (1913). *Zinc White and Zinc Grey :*—United Kingdom, £9,000 ; Canada, £1,400 ; Portugal, £1,300 ; Servia, £1,300 ; Roumania, £8,900 ; Russia in Europe, £12,200 ; United States, £7,600. *Ultramarine :*—Bulgaria, £1,500 ; Roumania, £2,900 ; Egypt, £1,600. *Lithopone :*—United Kingdom, £1,100 ; Sweden, £500 ; Italy, £2,250 ; Roumania, £650. *Prepared Blacks :*—Servia, £1,000 ; Roumania, £3,000. *Oil Varnish (without Addition of Resin, Turpentine, or Mineral Oil) :*—United Kingdom, £15 ; Italy, £100 ; Servia, £150 ; Roumania, £1,000. *Lac-varnish (with Resin, Turpentine, Mineral Oil, or Spirit) :*—United Kingdom, £150 ; Italy, £2,300 ; Greece, £800 ; Servia, £700 ; Bulgaria, £900 ; Roumania, £2,400 ; Russia in Europe, £100.

(c) *Exports from United Kingdom. Barytes :*—Canada, £300 ; Russia, £4,100 ; United States, £3,000. *White Lead :*—British India, £41,500 ; Sweden, £1,400 ; Denmark, £2,600 ; France, £100 ; Spain, £400 ; Portugal, £2,100 ; Russia, £22,600 ; Argentina, £56,100. *Zinc Oxide :*—British India, £6,800 ; Canada, £5,100 ; Norway, £100 ; Sweden, £700 ; France, £1,000 ; Spain, £500 ; Portugal, £100 ; Italy, £100 ; Dutch East Indies, £200 ; Brazil, £3,200 ; United States, £1,100. *Unenumerated :*—British India, £339,900 ; British South Africa, £133,000 ; British West Africa, £25,700 ; Australia, £253,000 ; Canada, £115,000 ; Norway, £22,900 ; Sweden, £32,300 ; Denmark, £19,700 ; France, £136,100 ; Portugal, £24,000 ; Spain, £57,800 ; Italy, £59,500 ; Greece, £7,200 ; Bulgaria, £600 ; Roumania, £7,400 ; Russia, £34,300 ; Egypt, £30,400 ; Dutch East Indies, £17,000 ; China, £52,000 ; Japan, £80,600 ; Brazil, £116,700 ; Uruguay, £16,000 ; Argentina, £122,600 ; Chile, £64,000 ; United States, £89,900 ; Mexico, £9,800.

Determination of peroxide in commercial lead oxide. Dean. *See* VII.

PATENTS.

Printing ink. M. Wolff, London. Eng. Pat. 4419, Feb. 20, 1914.

A CHEAP mineral base of kieselguhr (25 to 35 parts), barytes, or the like, is ground to an impalpable powder in a mill with rosin oil (20 to 30 parts), petroleum (20 to 30 parts), vegetable or carbon black (10 to 15 parts), and aniline dyestuffs (3 to

8 parts), without the addition of glycerin, glucose, or linseed oil, and without the application of heat or pressure.—C. A. M.

Varnish [for fabrics]. J. H. Hardcastle and A. H. Taylor, London. Eng. Pat. 13,100, May 28, 1914.

A VARNISH for woven fabrics such as are used in the manufacture of aeroplanes, balloons, etc., consists of cellulose acetate, 1 to 2 ; acetone, 8 ; alcohol, 3 ; benzene, 3 ; chloroform, 1, and tri-chloroethylene, 4 parts. The varnish may be rendered more flexible by the addition of resorcinol diacetate, 0·5 part.—W. P. S.

Volatile and fusible products from wood ; Process of extracting ——. J. L. Dormon, New Orleans, La. U.S. Pat. 1,122,084, Dec. 22, 1914. Date of appl., Oct. 25, 1913.

AN inert gas (carbon dioxide) is circulated through a mass of the wood at a definite temperature (*e.g.*, the b. pt. of turpentine) until all substances volatile or fusible at that temperature have been separated and collected. The temperature of the gas may then be raised, and further extractions made in stages until all volatile and fusible constituents have been removed.—C. A. M.

XIV.—INDIA-RUBBER ; GUTTA-PERCHA.

Rubber ; Committee on exportation of ——. Board of Trade, Jan. 22, 1915.

THE Board of Trade have appointed the Lord Balfour of Burleigh, K.T., the Rt. Hon. Russell Rea. M.P., and Mr. Henry Birchenough, C.M.G., to be a Committee to consider and advise on all questions relating to the export of rubber from the United Kingdom and from British Possessions. The Secretary to the Committee is Mr. J. K. Grebby, to whom all communications should be addressed at the Westminster Palace Hotel, London, S.W.

Sulphur in rubber ; Determination of ——. R. Gaunt. Analyst, 1915, 40, 9—11.

THE rubber (0·2 to 0·3 grm.) is placed in a small tube of hard glass, closed at one end, which is introduced into the middle of a combustion tube (30 to 35 cm.), drawn out at the rear end and connected with two small absorption flasks each containing 25 c.c. of 20 vol. hydrogen peroxide, whilst a loose plug of platinised asbestos is placed in front of the constriction. The part immediately below the mouth of the inner tube is gently heated, while a current of dry oxygen is drawn through the combustion tube, until the rubber no longer evolves gaseous products (which should burn at the mouth of the inner tube with a luminous but smokeless flame). Stronger heat is then applied until all carbon is burnt. The sulphur dioxide absorbed by the hydrogen peroxide is determined by titration or gravimetrically, a correction being made for any sulphuric acid originally present in the peroxide. In the case of rubber rich in mineral matter, sulphates in the ash are also determined. The results obtained as described in 90 mins. agree closely with those given by the method of Carius.—C. A. M.

XV.—LEATHER ; BONE ; HORN ; GLUE.

Gambier ; Note on the analysis of cube ——. H. G. Bennett. Collegium (London), 1915, 1, 13.

FOR analytical purposes cube gambier should be treated as a dry material and not as an extract,

owing to the difficulty of filtration and to the amount of insoluble matter present. Better results are thus obtained, and the filtration is more rapid. Soaking over-night is unnecessary, and hot water is used from the commencement of the extraction, which takes only a short time.—F. C. T.

XVI.—SOILS ; FERTILISERS.

Soil ; Partial sterilisation of —— by volatile and non-volatile antiseptics. W. Buddin. J. Agric. Sci., 1914, 6, 417—451.

RUSSELL and other investigators have shown the general effects of partial sterilisation of soils by volatile antiseptics and heat (see this J., 1913, 1136 ; 1914, 560), and the author now records the action of benzene, cyclohexane, hexane, aliphatic alcohols (methyl to amyl alcohol), ether, acetone, chloroform, formaldehyde, toluene, phenol, cresol, quinone, quinol, pyridine, calcium sulphide, sulphur, sodium fluoride, and sodium chloride. The characteristic effects of true partial sterilisation were found to be produced by a large number of antiseptics, *i.e.*, the number of bacteria at first decreased and then increased largely, protozoa and nitrifying organisms were killed, an initial increase of ammonia content was followed by a considerable increase in ammonia formation, and no increase in dose caused any change in the results obtained once true partial sterilisation had been attained. The intensity of the effect decreased gradually from that of the powerful non-volatile substances, through cresol (*M*/50 dose) and formaldehyde, to the more volatile, and less potent, substances, respectively, until finally the action of merely spreading out the soil in a thin layer was reached. Volatile antiseptics, though effective in increasing the productive capacity of a soil under laboratory and pot culture conditions, are unsuitable for application on a large scale.—W. P. S.

Soil ; Increased nitrate content of a —— when subjected to temporary drying in the laboratory. W. Buddin. J. Agric. Sci., 1914, 6, 452—455.

SOIL dried by spreading out in a thin layer for 24 hours, then moistened, and submitted to incubation, was found to contain from two to three times more nitrate than another portion which had been kept moist before incubation. This increased amount of nitrate in the dried soil is not due to absorption of ammonia from the atmosphere, but to the formation of more nitrate from the residues in the soil, in spite of the fact that the numbers of bacteria are not increased.—W. P. S.

Soil ; Evaporation of water from ——. B. A. Keen. J. Agric. Sci., 1914, 6, 456—475.

THE evaporation of water from the " sand " and " silt " fractions of soil, from china clay, and from ignited soil, can be explained by the known laws of evaporation and diffusion, but the evaporation of water from the soil itself is more complex, the relation between the soil and the soil water being of a different and closer nature than in the case of sand. The effect is not due to the soluble humus, but probably in part, if not mainly, to the colloidal properties of the clay fraction of the soil. The subject is also discussed from a mathematical point of view.—W. P. S.

Calcium carbonate ; Protective action of —— for A. chroococcum, against magnesium carbonate. C. B. Lipman and P. S. Burgess. J. Agric. Sci., 1914, 6, 484—498.

THE effects of calcium and magnesium carbonates on nitrogen fixation by *A. chroococcum* in soils

ind in solution were examined. Calcium carbonate
ip to 2% concentration in mannitol solution
ultures acted solely as a stimulant, whilst the
presence of more than 0·1% of magnesium
arbonate had a decided toxic effect. In soil
ultures, however, quantities of calcium carbonate
arger than 1·4% had a slight toxic action,
ind magnesium carbonate was more toxic than
n solution cultures, 0·1% being sufficient to
nhibit the fixation of nitrogen. Calcium carbonate
xercised a protective action in solution and soil
ultures for *A. chroococcum* against the toxic
properties of magnesium carbonate ; in the case
of soils, the best ratio was found to be 1·5% $CaCO_3$
o 0·1% $MgCO_2$.—W. P. S.

Fertilizers. Board of Trade Bulletin No. 56.

THE value of certain descriptions of fertilizers
(exclusive of potash compounds) exported from
Germany, Austria-Hungary, and the United King-
dom to all destinations in a recent year was as
follows :—*From Germany* (1912) :—Basic slag,
£1,368,200 ; sulphate of ammonia, £702,800 ;
superphosphates, £984,200 ; other manures,
£315,200 ; total, £3,370,400. *From Austria-Hun-
gary* (1913) :—Basic slag, £5,200 ; sulphate of
ammonia, £327,000 ; superphosphates, £9,200 ;
other manures, £104,000 ; total, £445,400. *From
United Kingdom* (1913) :—Basic slag, £262,000 ;
sulphate of ammonia, £4,390,500 ; superphos-
phates, £166,300 ; other manures, £926,700 ; total,
£5,745,500.

As regards exports of basic slag, Germany
holds an overwhelmingly strong position in the
Netherlands, Italy, and Russia. In New Zealand
we do the larger part of the trade, but German
competition is strong in the smaller Colonial
markets. In Norway, Sweden, and Denmark we
have most of the trade. We have a good share
of the trade in France, Spain, and Portugal, but
our share might well be increased in the United
States.

Two-thirds of Germany's exports of sulphate of
ammonia go to the Netherlands and Belgium.
German and Austrian competition is keen in the
Italian market, but elsewhere, particularly in
Ceylon, France, Portugal, Spain, Dutch East
Indies, and the United States, the United Kingdom
holds a very strong position. There would appear
to be opportunities for extending our sales of
sulphate of ammonia in the Netherlands, Belgium,
France, Italy, the Dutch East Indies, and Brazil.
In the chief markets, with the exception of New
Zealand, the British Dominions take more super-
phosphates from Germany than from the United
Kingdom. In Spain, France, and Denmark we
, do a fair trade, which might be increased, but
elsewhere, particularly in the Russian and United
States markets, the United Kindom is hardly
represented. Most of the Austrian superphos-
phates go to Russia. The United Kingdom holds
the bulk of the trade in other manures (bone
meal, animal blood, artificial guano, etc.), with
France, Portugal, United States, India, Ceylon,
and the British Dominions generally. Germany
has the bulk of the trade in Sweden, Switzerland,
Russia, and Hawaii, while German competition is
keen in Netherlands, Belgium, and the United
States. Austria-Hungary takes the bulk of the
trade in Italy and Roumania, and competes
successfully in Russia.

Tri-ammonium citrate. Hall. *See* VII.

Composition and analysis of lime-sulphur sprays.
Ramsay. *See* XIXB.

PATENTS.

*Electrochemical process for producing nitrogen
compounds.* U.S. Pat. 1,118,993. *See* VII.

*Insecticides for agricultural and horticultural pur-
poses.* Eng. Pat. 12,802. *See* XIXB.

XVII.—SUGARS; STARCHES; GUMS.

*Cane sugar factory ; Chemical control in the ——,
using boiling-house balances of both sucrose and
total solids.* H. Johnson. Report of Committee
on Boiling-house Balances to the Hawaiian
Sugar Planters' Assoc. Intern. Sugar J., 1915,
17, 27—31.

A BALANCE-SHEET of the total solids (using the
apparent dry substance), as suggested by Deerr
(this J., 1913, 802), may serve as a useful check
upon the customary sucrose balance-sheet. In
constructing it, the debit side is represented by
the solids (soluble and insoluble) entering in the
raw juice and in the lime added for defecation ;
while on the credit side appear the soluble and
insoluble solids present in the sugars, the molasses,
and the press-cake. together with the undeter-
minable loss of solids occurring during manu-
facture. The insoluble matter in the sugars,
molasses, and juices may be ascertained periodically
in average samples, and determinations made by
members of the Committee have given the follow-
ing results: Sugars, 0·1 ; molasses, 0·5 ; and
mixed juice, 0·53%, which amounts are deducted
from the value for the total solids found by the
Brix hydrometer in the case of the juices and
molasses, and by desiccation in that of the sugars.
For the construction of the sucrose balance,
and the determination of the sucrose, it is recom-
mended that the method already adopted by the
Hawaiian Sugar Planters' Association (Bull.
No. 35 ; this J., 1911, 145) be retained until a
more accurate one is devised.—J. P. O.

*Carbohydrates ; Determination of ——. IV. Pre-
sence of free pentoses in plant extracts and the
influence of other sugars on their determination.*
W. A. Davis and G. C. Sawyer. J. Agric. Sci.,
1914, 6, 406—412. (See this J., 1913, 1024 ;
1914, 657).

PLANT extracts contain substances which are
soluble in 80% alcohol, are not precipitated by
basic lead acetate, are not fermented by ordinary
yeasts, and possess a certain reducing power
after all other sugars have been fermented ;
this reducing power (calculated as due to a mixture
of arabinose and xylose) corresponds with a
quantity of pentose practically identical with that
calculated from the weight of phloroglucide
obtained by subjecting the purified solution to the
ordinary Kröber-Tollens distillation process (this
J., 1901, 396 ; 1902, 875). These facts can only
be explained by assuming that free pentoses are
present. To determine small amounts of pentose
in the presence of large quantities of other
sugars, the latter should be fermented before
applying the distillation process, since sucrose
and certain hexoses yield small quantities of an
insoluble phloroglucide. The pentose may, how-
ever, be determined with a fair degree of accuracy
by the ordinary distillation process or by the
reducing power after fermentation. Leaves of
various plants (mangolds, turnips, carrots,
potatoes, etc.) were found to contain from 0·3 to
1% of pentose, calculated on the dry material.
—W. P. S.

*Maltose ; Hydrolysis of —— by hydrochloric acid
under the Herzfeld conditions of inversion.*
W. A. Davis. J. Agric. Sci., 1914, 6, 413—416.

THE author and A. J. Daish have stated previously
(this J., 1913, 1024) that maltose is hydrolysed

partially by hydrochloric acid, and, in reply to criticisms of this statement (Kluyver, Biochem. Suikerbepalingen, 1914, 223), results of experiments are now recorded showing that, using a 1% solution of maltose, about 2% of the sugar is hydrolysed by treatment with hydrochloric acid under Herzfeld conditions. In determining sucrose in plant extracts, where maltose is likely to be present, the inversion should therefore be made by boiling with citric acid, which is without effect on the maltose (*loc. cit.*).—W. P. S.

XVIII.—FERMENTATION INDUSTRIES.

Manganese ; Non-poisonous nature of —— [*towards yeast*]. T. Bokorny. Chem.-Zeit., 1914, **38**, 1290.

MANGANOUS salts, unlike those of the other heavy metals, are not toxic. The budding of yeast was found to proceed quite normally in nutrient liquids containing 1% of manganous sulphate, whereas it was completely arrested in presence of 1% of ferrous sulphate. Yeast which had been steeped for 24 hours in a 1% solution of manganous sulphate and then well washed, contained no manganese, but yeast which had been similarly treated with solutions of ferrous and cobalt salts could not be washed free from the respective metals. The innocuous character of manganous salts is attributed to the fact that, unlike the other heavy metals, manganese does not combine chemically with the protoplasm (see this J., 1915, 44).—J. H. L.

XIXA.—FOODS.

Cheese from " heated " milk ; Manufacture of ——. M. Benson. J. Board Agric., 1915, **21**, 878—889.

To obtain a typical cheddar cheese from pasteurised milk, the pasteurising temperature should not be higher than 190° F. (88° C.) when the milk is heated very rapidly, or 170° F. (77° C.) when the period of heating is from 15 to 30 mins. A blue-veined cheese of good quality was obtained when the milk was heated for about 15 mins. to 190°—200° F. (88°—93° C.). Cheeses prepared from heated milk contained : water, 33·61 to 36·22 ; fat, 32·36 to 34·53 ; insoluble nitrogen (probably unaltered casein), 2·49 to 2·91%. In the case of very rapid heating, the number of organisms in the milk was not effectively reduced below 170° F. (77° C.), but at this point the number was reduced to one-fiftieth of the total and at 180° F. (82° C.) to one eighty-eighth, whilst at 200° F. (93° C.) practically all the organisms were destroyed. There was a much greater reduction when the milk was maintained at 150° F. (66° C.) for 15 mins. than when it was heated very rapidly to 170° F. (77° C.).—W. P. S.

Margarine ; Use of hydrogenised fish oil in the manufacture of ——. J. Klimont and K. Mayer. Z. angew. Chem., 1914, **27**, 645—648.

THE chief objections against the use of hydrogenised fish oil in the manufacture of margarine are that the production of the crude fish oil is not under proper control, that the disagreeable odour may reappear when the hydrogenised oil is kept for a long time, that the hydrogenised oil may contain small quantities of nickel, and that it has a higher melting point than any of the fats hitherto used for foods and hence would probably not be easily digested. The authors were unable to detect nickel in samples of hydrogenised oil examined by them ; hence this test could not be relied upon for the detection of hydrogenised fish oil in oleomargarine. The following test is proposed :—2—3 grms. of the sample is melted, and dissolved in acetone to a total volume of 50 c.c. After standing for 12 hours at the ordinary temperature, the crystals which separate are filtered off, dried, and weighed. Oleomargarine yields 12—13% of crystals of m. pt. 45°—47° C. In the case of artificial mixtures of oleomargarine with hydrogenised fish oil and rape oil, the portion crystallising from acetone was in all cases considerably greater than 12—16%, which may be taken as the limits for genuine oleomargarine. It was possible by this test to detect 3·5% of hardened fish oil when this was added, together with 5·5% of rape oil, to oleomargarine.

By repeated fractional crystallisation of oleomargarine from acetone, an oil which became only semi-solid when cooled below 0° C. was obtained. This had an iodine value (51·6) lower than that of triolein, a result which is in accordance with the view that oleomargarine consists largely of mixed glycerides of oleic and other fatty acids.—A. S.

Feeding stuffs (oilcake and bran). Board of Trade Bulletin No. 76.

THE following statement shows, for a recent year, the value of feeding stuffs (oilcake and bran) exported from Germany, Austria-Hungary, and the United Kingdom, respectively, to all destinations :—*From Germany* (1912) :—Oilcakes, oilcake meal, almond bran (dried and powdered residue of oil-extracted almonds), £1,702,900 ; bran and rice waste, £132,350 ; total, £1,835,250. *From Austria-Hungary* (1913) :—Linseed and other oilcakes and solid residues from the manufacture of oil (including almond bran), £407,755 ; bran and rice offals, £201,235 ; total, £608,990. *From the United Kingdom* (1913) :—Oilseed cakes of all sorts, £354,340 ; bran and other corn and grain offals (including rice meal and dust), £1,256,450 ; total, £1,610,790.

Each of the three countries exports a certain amount of these feeding stuffs to the other two. The extent of this trade in a recent year was as follows :—*From Germany* (1912) :—To United Kingdom, £392,650 ; to Austria-Hungary, £146,150. *From Austria-Hungary* (1913) :—To United Kingdom, £7,980 ; to .Germany, £573,300. *From United Kingdom* (1913) :—To Germany, £759,200 ; to Austria-Hungary, £400.

The bulk of the oilseed cake trade is concentrated in Western European countries. The United Kingdom leads in the French, Russian, and United States markets, and does a fair trade with Denmark and the Netherlands ; but elsewhere the trade is in German hands, with the exception of the Italian market, which is almost entirely supplied by Austria-Hungary.

Presence of free pentoses in plant extracts and the influence of other sugars on their determination. Davis and Sawyer. See XVII.

Hydrolysis of maltose by hydrochloric acid under Herzfeld conditions of inversion. Davis. See XVII.

PATENTS.

Soya beans ; Treatment of —— and the production of a food preparation therefrom. J. Friedman, London. Eng. Pat. 121, Jan. 2, 1914.

To remove its unpleasant flavour, soya bean flour is heated to 120°—300° C. while being continuously agitated. Soya bean flour for bread-making, for example, is heated at 155° C. for about 70 minutes.—W. P. S.

Milk preparation ; Dried ——. E. P. Carpenter, London. Eng. Pat. 1409, July 1, 1914.

SEPARATED milk is evaporated to a density of 16° (sp. gr. 1·121) and emulsified with an edible oil or fat, at a maximum temperature of 130 F. (55° C.). The evaporation is continued in a vacuum for 20 min. and the residue dried. The dry powder contains from 5 to 30% of fat.—J. H. J.

Milk ; Apparatus for drying ——. J. D. McIntyre, New York. Assignor to W. de Shetley, Chicago, Ill. U.S. Pat. 1,122,142, Dec. 22, 1914. Date of appl., Aug. 1, 1913.

THE vessel containing the milk has a slot in the bottom admitting hot air. An agitator within the vessel is worked at a high speed, *e.g.*, by a friction drive, during the evaporation of the milk to a doughy consistence, and later, during the conversion of the doughy mass into a granular condition, at a lower speed by a positive drive.
—J. H. J.

Foodstuffs, beverages, and the like ; Preservation of ——. J. Milburn, London. Eng. Pat. 9024, April 9, 1914.

FOODSTUFFS, beverages, etc., are treated with from 0·05 to 0·1% of their weight of a mixture of salicylic, benzoic, and boric acids, sodium sulphite, and sodium sulphocarbolate ; borax or a borate may be used in place of the boric acid, and sulphurous acid or sodium bisulphite instead of sodium sulphite.—W. P. S.

Desiccated milk ; Process of producing ——. A. A. Dunham, Bainbridge, N.Y., U.S.A. Eng. Pat. 27,015, Nov. 24, 1913. Under Int. Conv., April 11, 1913.

SEE U.S. Pat. 1,074,419 of 1913 ; this J., 1913, 1027.*

Cooling hot or molten fats and fatty emulsions and the like. Eng. Pat. 19,863. *See* XII.

XIXв.—WATER PURIFICATION ; SANITATION.

Silicic acid in natural waters ; Determination of ——. L. W. Winkler. Z. angew. Chem., 1914, 27, 511—512.

THE method depends upon the yellow coloration produced by silicic acid with ammonium molybdate in presence of hydrochloric acid : 100 c.c. of the water, contained in a beaker, is treated with 1 grm. of powdered ammonium molybdate and 5 c.c. of 10% hydrochloric acid, and in a second similar beaker, 105 c.c. of the water is treated with potassium chromate solution (0·530 grm. K₂CrO₄ in 100 c.c.), until the yellow colour matches that of the other solution. The number of c.c. of chromate solution used, when multiplied by 10, gives the quantity of SiO₂ in mgrms. per litre. The results are as accurate as those obtained by the tedious gravimetric process.—A. S.   •

Sulphurous acid in the atmosphere ; Detection of —— by means of mercury salts. Denigès. Bull. Soc. Pharm. Bordeaux, April, 1914. Ann. Chim. Analyt., 1915, 20, 10—11.

THE end of a glass rod is moistened with a solution of mercuric sulphate (5 grms. of mercuric oxide in 20 c.c. of sulphuric acid of sp. gr. 1·84 and 100 c.c. of water) and exposed to the atmosphere. In the presence of sulphurous acid a crystalline deposit of stellar formation is produced on the rod. Or a solution of mercuric acetate (5 grms. of mercuric acetate in 100 c.c. of water and 1 c.c. of glacial acetic acid) may be used, the crystals produced being spherical masses. With mercurous nitrate (5 grms. of mercurous nitrate in a mixture of 5 c.c. of nitric acid of sp. gr. 1·39, and 50 c.c. of water) a brownish deposit consisting of a mixture of metallic mercury and mercurous sulphate, which only exceptionally is crystalline, is obtained.
—C. A. M.

Lime-sulphur sprays ; Composition and analysis of ——. A. A. Ramsay. J. Agric. Sci., 1914, 6, 476—483.

LIME-SULPHUR solution contains calcium disulphide in addition to the compounds mentioned previously (this J., 1914, 662). The solution may be analysed as follows : 50 c.c. of the concentrated lime-sulphur solution is diluted to 250 c.c. ; 25 c.c. of this solution is titrated with $N/10$ iodine solution until the yellow colour is discharged, and the titration is continued until a faint yellow coloration is obtained. The second titration gives the quantity of thiosulphate present. The titrated solution is filtered, the filtrate is slightly acidified with hydrochloric acid, barium chloride is added, and the resulting barium sulphate collected and weighed ; this gives the quantity of sulphur present as sulphate and sulphite. Free sulphur is determined by extracting 10 c.c. of the diluted solution with carbon bisulphide, and total sulphur by oxidising 10 c.c. of the diluted solution with sodium peroxide, acidifying the solution with hydrochloric acid, adding a small quantity of potassium iodide, and precipitating with barium chloride. The total lime is found by treating 10 c.c. of the diluted solution with iodine solution, separating the sulphur by filtration, and precipitating the lime as oxalate. The sulphur (a) present as hydroxyhydrosulphide and disulphide is found by subtracting the sum of the sulphur present as free sulphur, sulphate, sulphite, and thiosulphate from the total sulphur ; the lime (b) occurring as hydroxyhydrosulphide and disulphide by subtracting that present as sulphate, sulphite, and thiosulphate, from the total lime. If x =lime in combination as hydroxyhydrosulphide, then b—x =lime in combination as disulphide ; $x \times 0·5714$ will be the sulphur in combination as hydroxyhydrosulphide, and $(b—x) \times 1·1428$ the sulphur as disulphide. The value of b—x is found from the equations :

$$x \times 0·5714 + (b—x) \times 1·1428 = a,$$
$$\text{and } x = \frac{(b \times 1·1428)—a}{0·5714}.$$ —W. P. S.

PATENTS.

Filtering water ; Apparatus for ——. M. Deacon and W. Gore, London. Eng. Pat. 27,885, Dec. 4, 1913.

IN sand filters for dealing with large volumes of water (see Eng. Pats. 14,487 of 1910 and 29,301 of 1911 ; this J., 1913, 221), the sand is divided into several units capable of being worked separately. Each unit has around its base a set of bifurcated pipes leading into a main pipe beneath the unit. Before entering the main, each branch pipe is bent round on itself and terminates in a nozzle delivering into an upright pipe connected to the main drain ; at the bottom of the bend water under slight pressure is introduced to keep the sand in a state of flow. The dirty sand is withdrawn through these pipes and carried to a washing apparatus in the centre of the filter, where it is lifted by a bucket conveyor and fed into a hopper-mouthed pipe containing baffles. Here the falling sand meets the water to be filtered passing upwards and is washed by it. The washed sand and the water

travel along a pipe at the top of the filter and are delivered over the centre of each unit. The filtered water passes out through a number of perforated pipes in the base of each unit which are connected to a main collector.—J. H. J.

Water purification [removing gasolene, etc.]. C. Ellis, Montclair, N.J., Assignor to Ellis-Foster Co. U.S. Pat. 1,121,994, Dec. 22, 1914. Date of appl., Aug. 7, 1914.

WASTE water from garage washings, containing small quantities of gasolene or other inflammable oil, is passed through a bed of sawdust or other porous material impregnated with a non-volatile oil.—J. H. J.

Sewage disposal. R. W. Pratt, Cleveland, Ohio. U.S. Pats. 1,122,155 and 1,122,156. Dec. 22, 1914. Dates of appl., March 16 and June 30, 1914.

THE sewage passes through either an unobstructed channel at a regulated speed, or a channel with walls capable of being adjusted so as to give a constant rate of flow through the channel. The sludge collects in a chamber, which is heated and has a contracted upper portion forming an outlet, with a shelf inclined away from the outlet for receiving matter rising to the surface. The remaining sludge is run out on to a sand bed in a ventilated and heated chamber with a translucent roof.—J. H. J.

Dynamite fumes, gases and dust in the atmosphere caused by blasting, drilling, and the like in mines; Method for consuming by fire ——. W. Alderson, Kimberley, S. Africa. Eng. Pat. 20,258, Sept. 8, 1913.

TRUCKS or pans carrying fires are run on rails or wires through the working places in the mine before and after the shots are fired, to consume the dust and fumes arising from the drilling or explosion. Explosive mixtures of gas and air are first removed by ventilation.—W. H. C.

Suspended impurity in the air; Apparatus for measuring the amount of ——. J. S. Owens, London. Eng. Pat. 8725, April 7, 1914.

THE air is drawn by an aspirator through a small disc of filter-paper. held between two perforated plugs, and the quantity of impurity is determined by comparing the shade of the discoloration with a scale of standard discolorations.—O. E. M.

Insecticides for agricultural and horticultural purposes. W. Calderwood and A. E. Webb, London. Eng. Pat. 12,802, May 25, 1914.

THE insecticide consists of 60% of soft soap. 38% of anhydrous sodium carbonate, and 2% of powdered camphor, pyrethrum, bitter apples, aloes, gentian, quassia, hyssop, or senna, or mixtures of these.—W. P. S.

XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.

Synthetic drugs in Great Britain. [Preparation of phenacetin and β-eucaine.] J. F. Thorpe. Nature, Jan. 28, 1915, 593—594.

AT the request of the Admiralty, the Imperial College of Science and Technology has been engaged recently in the preparation of phenacetin and β-eucaine, which had not previously been manufactured in this country. To prepare phenacetin, acetanilide was nitrated, the p-nitro compound was treated with alkali to produce the sodium salt of p-nitrophenol, which was converted by means of ethyl bromide into p-nitrophenetol, and this was reduced and the product acetylated. β-Eucaine

was obtained by condensing acetone with oxalic acid and ammonia to form the hydrogen oxalate of diacetoneamine, condensing this with paraldehyde to produce the cyclic vinyl-diacetoneamine, reducing by means of sodium amalgam to a mixture of the *cis* and *trans* forms of the trimethyl-hydroxypiperidine, treating with sodium amylate to produce the *cis* form only of this compound, and treating with benzoyl chloride and finally with hydrochloric or lactic acid to obtain the corresponding salt of β-eucaine.

Apomorphine; Delicate reaction for ——. L. Grimbert and A. Leclère. J. Pharm. Chim., 1915, 11, 23—24.

THE characteristic blue coloration produced by the oxidation of apomorphine hydrochloride solutions by atmospheric oxygen can be intensified as follows : 5 c.c. of the solution is mixed with 5 drops of a saturated solution of mercuric chloride and 5 drops of 10% sodium acetate solution, boiled, cooled, and shaken with amyl alcohol, which dissolves the blue substances. One part of apomorphine in 500,000 can be detected in this way. (See also this J., 1915, 100.)—F. SHDN.

Tormentol, a principle extracted from Potentilla tormentilla Neck. A. Goris and C. Vischniac. Comptes rend., 1915, 160, 77—80.

A CRYSTALLINE principle, tormentol, $C_{33}H_{50}O_{10}$, has been isolated from the roots of the tormentil or septfoil. It crystallises in fine needles with 5 mols. H_2O, melts at $227°$—$228°$ C., and is optically active ($[a]_D = +10.78°$ in alcoholic solution). It is saturated and neutral, possesses the properties both of an alcohol and an ester, but does not react with reagents for ketones. It is soluble in alcohol, acetone, and acetic acid, insoluble in water and ether. On saponification with alcoholic potassium hydroxide, tormentol yields an acid, m. pt. 280° C., and an alcohol, m. pt. 310° C.—G. F. M.

Cineol in oil of eucalyptus; Determination of ——. J. L. Turner and R. C. Holmes. Pharm. J., 1915, 94, 60—63.

THE determination of cineol in eucalyptus oils by means of its addition compound with arsenic acid (see Watson Smith, this J., 1902, 1096, 1194) is recommended. The procedure is analogous to that followed in the known phosphoric acid process, and the method is superior to the resorcinol method (this J., 1908, 90). It can be applied directly to all cineol-bearing oils and gives results agreeing within 2%. With oils containing less than 50% of cineol, a known volume of the latter should be added first ; whilst if the oil be so rich in cineol that the arsenic acid addition compound sets to a hard mass, 5 c.c. of petroleum ether is added.
—F. SHDN.

Blue hydrocarbon; The ——, occurring in some essential oils. A. E. Sherndal. J. Amer. Chem. Soc., 1915, 37, 167—171.

A CONNECTION is deduced between the green or blue colour of the essential oils of chamomile, wormwood, and cubebs and the blue fraction yielded between 275° and 300° C. by many other oils when distilled. The addition of a little sulphuric acid to an acetic anhydride solution of oil of gurjun balsam produces an intensely blue oil which is volatile in steam. Blue or violet colours are similarly given by the oils of amyris and guaiac-wood, but not by those of santal and cedar-wood. The reaction is suggested as a test for adulterants in oils of the last type. A freshly steam-distilled blue fraction was shaken with 63% sulphuric acid, and from this solution the blue extract was transferred in turn to petroleum spirit, 85% phosphoric acid, and ether. The intensely

blue liquid thus obtained amounted to 0·28% of the original oil. It dissolved unchanged in most organic solvents and in strong inorganic acids, and was precipitated from the latter upon dilution with water. The substance, for which the name " azulene " is proposed, appears to be a highly unsaturated hydrocarbon of the formula, $C_{15}H_{18}$.

—J. R.

Dihydroxystearic and dihydroxybehenic acids; Action of fused potassium hydroxide on ——. H. R. Le Sueur and J. C. Withers. Chem. Soc. Trans., 1914, 105, 2800—2819.

DIHYDROXYSTEARIC acid when fused with potassium hydroxide yielded *a-hydroxy-a-octylsebacic acid*, $CO_2H.C(OH)(C_8H_{17}).(CH_2)_7.CO_2H$, m. pt. 111°—112° C., and this when oxidised with potassium permanganate in acetone solution gave *β-ketomargaric acid*, $C_8H_{17}.CO.(CH_2)_7.COOH$, m. pt. 78·5° C., and when heated alone above its melting point gave two unsaturated acids, $C_{18}H_{32}O_4$, which by addition of hydrogen were converted into *a-octylsebacic acid*, m. pt. 71·5°—72·5° C. The constitution of β-ketomargaric acid and hence of a-hydroxy-a-octylsebacic acid was elucidated by converting its oxime into the corresponding amides by heating with concentrated sulphuric acid, and hydrolysing these by heating with hydrochloric acid, when *n*-nonoic acid, octylamine, azelaic acid and *n*-amino-*n*-octoic acid were obtained. Dihydroxybehenic acid, obtained by the oxidation of erucic acid, yielded *a-hydroxy-a-octyldodecanedicarboxylic acid*, $CO_2H.C(OH).(C_8H_{17}).(CH_2)_{11}.CO_2H$, m. pt. 127°—128° C., when fused with potassium hydroxide. On oxidation this gave *μ-ketoheneicosoic acid*, m. pt. 89°—90° C., the oxime of which gave two amides on heating with concentrated sulphuric acid. The amides, on hydrolysis, yielded *n*-nonoic acid, octylamine, brassylic acid, and λ-aminolauric acid. The intramolecular changes brought about during fusion with potassium hydroxide involve the migration of the group, C_8H_{17}, from one carbon atom to another adjacent to it. No previous example of such movement of a heavy group within a molecule has been recorded in an aliphatic compound.—T. C.

Sterile solutions of common salt for hypodermic injections; Rapid method of preparing ——. Tœge. Münch. med. Wochenschr., 1914, 1325. J. Pharm. Chim., 1915, 11, 32.

A SOLUTION of hydrochloric acid is heated to boiling and neutralised by dilute sodium carbonate solution whilst still hot, using phenolphthalein as indicator.—F. SHDN.

Medicines, comprising drugs and medicinal preparations. Board of Trade Bulletin.

THE following statement shows for a recent year the value of drugs and medicinal preparations exported from Germany, Austria-Hungary, and the United Kingdom, respectively, to all destinations, so far as the particulars are available :—

Exported from Germany (1912) : Opium, £24,500 ; Peruvian bark, rhubarb roots, and medicinal berries, leaves, flowers, etc., £237,100 ; quinine, quinine salts, and compounds, £264,600 ; collodion and celloidin, £7,700 ; chloroform, chloral hydrate, £18,500 ; liquorice juice, £18,600 ; artificial balsams, extracts, waters and the like, not sweet smelling, £35,000 ; juices of fruits and plants, for medicinal use, containing ether or alcohol, £150 ; prepared medicaments and other pharmaceutical products, not otherwise mentioned, £895,500 ; chemical products, not otherwise mentioned, for medicinal uses, £742,500 ; total, £2,244,150.

Exported from Austria-Hungary (1913) :—Medicines, prepared, and all substances which by

inscriptions on their labels or wrappers, etc., purport to be medicines (including veterinary medicines), opium, etc., £191,600.

Exported from the United Kingdom (1913) :— Cocaine and cocaine salts, £1,000 ; morphia and morphia salts, £193,400 ; opium, dried, and powdered in the United Kingdom, £12,400 ; quinine and quinine salts, £72,600 ; medicines, unenumerated, £2,072,300 ; total, £2,351,700.

Though the German and British exports of medicines, etc., are about equal in value, there are considerable differences in their distribution. Thus, while the United Kingdom holds a practically unchallenged position in the British Colonial and Chinese markets, Germany holds almost a similar position in the Russian and to a somewhat smaller extent in the Swedish, Swiss, and United States markets. In France and the South American markets we are holding our own, the two countries sending about equal amounts to the markets in question. In many of the other markets, however, Germany has established a long lead, particularly in Norway, Sweden, Denmark, Netherlands, Belgium, Switzerland, Spain, Italy, Roumania, the Balkan States, and Argentina. Exports of medicines from Austria-Hungary are insignificant when compared with those of Germany or the United Kingdom. The principal markets for Austrian medicines are found mainly in neighbouring countries, Switzerland, Italy, Russia, Roumania, Bulgaria, etc., though certain quantities are also sent to the United Kingdom and the United States.

In 1912 the principal German markets for *opium* were the United States, Russia, Holland, and Switzerland ; for *Peruvian bark, rhubarb roots, and medicinal berries, leaves, flowers, etc.*, the United States, Russia, the United Kingdom, France, and Switzerland; for *quinine and its salts and compounds* the United States, Russia, Italy, and the United Kingdom ; for *collodion and celloidin*, France, Holland, and Russia ; for *chloroform and choral hydrate*, Russia, Argentina, Belgium, Australia, Japan, Italy, and the United Kingdom ; for *liquorice juice*, Denmark, Holland, Sweden, Norway, and Belgium.

Volatile and essential oils. Board of Trade Bulletin No. 100.

THE value of volatile and essential oils exported from Germany in 1912 was £482,500 ; from Austria-Hungary (1913), £78,270 ; and from the United Kingdom (1913), £111,500. A considerable amount of trade in these oils is carried on between the three countries. Thus, Germany in 1912 exported volatile and essential oils to the value of £52,050 to Austria-Hungary and £51,400 to the United Kingdom. Similarly, Austro-Hungarian exports to Germany and the United Kingdom were valued at £50,170 and £3120, respectively, in 1913, while the value of the exports from the United Kingdom to Germany and Austria-Hungary in the same year amounted to £20,800 and £1800 respectively.

Excluding the trade referred to above, the value of the exports to 38 of the principal Colonial and neutral markets only, considered as a whole, reached the following amounts : from Germany (1912), £366,750 ; from Austria-Hungary (1913), £24,950 ; from the United Kingdom (1913), £86,600. The combined value of the German and Austro-Hungarian exports to these markets was about five times that of the exports from the United Kingdom. Only in the cases of Canada, Australia, and New Zealand do the exports from the United Kingdom exceed those from Germany. In all the other markets German or Austro-Hungarian exports are predominant, competition from the United Kingdom being greatest in France, Belgium, Switzerland, British India, and Japan.

The countries, formerly supplied by Germany and Austria-Hungary, which appear to offer the greatest scope for exploitation by United Kingdom manufacturers of essential and volatile oils are Russia, United States, France, Japan, Italy, South American countries, Mexico and Cuba, Scandinavia, British India, and Spain. In 1913 British trade was quite unrepresented in British West Africa, Portugal, Greece, Bulgaria, Servia, Egypt, Dutch East Indies, Philippines, Venezuela, Peru, Mexico, and Cuba.

Some properties of solutions of the boric acids in alcohol. Firth and Myers. *See* VII.

PATENTS.

Carbon tetrachloride; Process for making ——. C. J. Strosacker, Assignor to The Dow Chemical Co., Midland, Mich. U.S. Pat. 1,121,880, Dec. 22, 1914. Date of appl., June 20, 1911.

SULPHUR chloride is distilled with the fractions rich in carbon bisulphide, from crude carbon tetrachloride. Sulphur chloride and carbon bisulphide are added to the still residue, giving a fresh supply of distillate rich in carbon bisulphide.
—O. E. M.

Ethyl acetate; Manufacture of —— *from acetaldehyde.* Konsortium für Elektrochemische Industrie G. m. b. H. Ger. Pat. 277,188, June 13, 1913. Addition to Ger. Pat. 277,187.

IN the preparation of ethyl acetate from acetaldehyde by the process described in the chief patent (see Eng. Pat. 26,826 of 1913 ; this J., 1914, 666), the aluminium alkyl oxide catalyst is used in solution, preferably in ethyl acetate. The aldehyde may be added to the solvent used for dissolving the catalyst. (See also Eng. Pat. 26,825 of 1913 ; this J., 1914, 666.)—A. S.

XXII.—EXPLOSIVES; MATCHES.

Explosion of picric acid; Report on the circumstances attending an —— *which occurred at the factory belonging to Messrs. Henry Ellison, Ltd., at Heckmondwike, on Dec. 2, 1914.* A. Cooper-Key, H.M. Chief Inspector of Explosives. [Cd. 7774.]

As a result of the explosion ten men were killed and five injured. The factory comprised five buildings in which picric acid was manufactured by the wet process (nitration of sulphonated phenol) and four in which the acid was respectively dried, sifted, packed, and stored. The explosion originated in the sifting shed, in which there was also a mill for grinding crystals too large to pass through the revolving sieve. The quantity of picric acid in the sifting shed was about 700 lb., and the explosion was communicated sympathetically to the drying shed, 30 ft. distant, containing about 1 ton of picric acid. The packing shed and the portions of the magazine of lighter construction were also destroyed, but the picric acid contained therein did not explode or even take fire, although the hoops were stripped from the barrels. As a result of investigations in connection with previous explosions of picric acid (see this J., 1887, 835 ; 1900, 929), it had been decided that picric acid when free from metallic picrates would not explode without giving sufficient warning by fire to allow anyone in the vicinity to escape, and that a fire, in its initial stages, could be extinguished by water without much difficulty ; also that provided suitable sprinklers were fitted to every building or compartment liable to contain dry picric acid, and that the quantity present did not

exceed 2000 lb., the danger of a fire developing into an explosion was negligible. It is concluded that in the case under report the ignition of the picric acid was probably due to the accidental presence in the grinding mill of a nail, stone, or other hard foreign substance, and that the explosion was one of dust rendered more than usually violent by the circumstance that the dust contained within itself all the elements necessary to form an explosion. There was evidence that much inconvenience was caused in the sifting and grinding room by dust ; and on the day of the explosion a fairly strong wind was blowing almost directly into the door of the building, which, no doubt, was opened from time to time to clear the air.

In consequence of the explosion all licensed manufacturers of picric acid in the United Kingdom have been called upon to discontinue the process of dry grinding of large crystals and to take measures to prevent, as far as practicable, the formation of fine dust during sifting. Grinding of the crystals in water by means of edge-runners of granite working on a granite bed is suggested as a practical method ; or the use of aluminium rollers or runners might be tried.

Attention is drawn to the risk of dust explosions in the manufacture of trinitrotoluene, for which, owing to the insensitive character of the substance, no licence is required. It is suggested, also, that the explosion of collodion cotton of low nitrogen content at the Pegamoid factory, Edmonton, in 1905 (this J., 1905, 690) was a dust explosion.—A.S.

Nitrocellulose from cotton and wood celluloses. C. G. Schwalbe and A. Schrimpff. Z. angew. Chem., 1914, 27, 662—664. (See also this J., 1912, 954.)

COMPARATIVE nitration experiments were made with cotton and a series of typical wood celluloses. The commercial wood pulps were transformed into thin sheets of paper, which were dried at 95°—100° C. before nitration. The highest nitrate obtained from cotton contained 13·46% N, the highest from wood cellulose 13·34%. It was found possible to prepare from wood pulp a nitrocellulose with a solubility of 5—6% in ether-alcohol. Stabilisation by digestion with water under pressure produced a change in the constitution of the nitrocellulose, such that its solubility in ether-alcohol was materially increased ; the ordinary technical method of stabilisation was therefore adopted. No difficulty was experienced in removing the unstable products from the nitrocelluloses prepared from wood-pulp ; after suitable treatment these gave results conforming with the official specification by Bergmann and Junk's test (this J., 1905, 953), and were at least as stable as the cotton nitrocelluloses. In the nitration of thin paper, success depends on the structure of the latter : overbeaten fibres give bad results. In pulping nitrocotton, traces of copper, amounting in some cases to 0·050—0·058%, may be absorbed from the beater-knives, but without appreciable effect upon the stability test. In celluloid manufacture the product is sometimes bleached after nitration and pulping ; this operation was found to eliminate unnitrated cellulose and had a slight effect on the nitrogen-content, varying in either direction according to the origin of the material. Unstable sulphuric esters can be eliminated by boiling with dilute acid : 1% hydrochloric acid gave better results than dilute sulphuric acid, causing no decomposition of the nitrocellulose, and leaving a product of lower solubility and somewhat greater stability.—J.F.B.

Instrument for measuring flame velocities in gas and dust explosions. Morgan. *See* IIA.

Combustibles for explosives; Manufacture of——.
O. B. Carlson, Mansbo, Assignor to O. F.
Carlson, Stockholm, Sweden. U.S. Pat.
1,122,072, Dec. 22, 1914. Date of appl., June
15, 1911.

NITRATED resin and a nitro-compound are heated
together and the product nitrated.—O. E. M.

*Explosives; Plastic—— and method of manu-
facturing the same.* C. V. A. Herlin, Vinter-
viken, Sweden. Eng. Pat. 26,493, Nov. 18,
1913. Under Int. Conv., April 14, 1913.

SEE Fr. Pat. 465,771 of 1913; this J., 1914, 614.

*Method for consuming by fire dynamite fumes,
gases, and dust in the atmosphere caused by
blasting, drilling, and the like in mines.* Eng. Pat.
20,258. See XIXB.

XXIII.—ANALYTICAL PROCESSES.

*Titanous chloride; Use of—— in qualitative
analysis.* A. Monnier. Ann. Chim. Analyt.,
1915, 20, 1—4. (See also this J., 1903, 232, 762,
825; 1904, 503; 1905, 1192; 1907, 1165.)

TITANOUS chloride (0·8% solution) reduces hot
neutral or slightly acid solutions of platinum,
palladium, or iridium chlorides, yielding the
respective metals. It reduces cold solutions of
auric chloride, forming a blue solution with red
fluorescence and a grey-blue precipitate on stand-
ing. This test will detect gold in the presence of
platinum or iridium, but free hydrochloric acid
must be present to prevent precipitation of the
latter. With alkali tungstates acidified with
dilute hydrochloric or sulphuric acid, it gives an
intense characteristic blue coloration, whilst with
molybdates it produces a brown coloration chang-
ing to green or blue on standing or on heating.
It decolorises acid solutions of alkali vanadates;
the liquid becomes pale blue when heated. It
reduces solutions of chromates to chromium
salts, selenious acid to selenium, tellurous acid
to tellurium, and sulphites and thiosulphates
to sulphur. *Organic acids:*—Formates and
acetates are reduced, with the formation of violet
or violet-black basic salts. Alkali oxalates give
a yellow coloration, and a yellowish-brown pre-
cipitate on boiling; succinates a voluminous
violet-grey precipitate; and neutral tartrates a
grey precipitate. The intense violet coloration
given by solutions of alkali citrates is a sensitive
and distinctive test. After a few hours the surface
of the liquid is decolorised by oxidation, but at
the bottom the colour persists for several days.
Alkali lactates give a pale blue to violet-brown
coloration, the intensity of which rapidly
diminishes. Alkali benzoates give a voluminous
brownish-green precipitate; salicylates a yellowish-
green precipitate; and tannin (in aqueous
solution) a voluminous red-orange precipitate.
Citric acid can be detected in the presence of
formic, acetic, succinic, lactic, and benzoic acids
by the reagent, but oxalic and salicylic acids inter-
fere.—C. A. M.

*Tungsten; The separation of—— from molyb-
denum.* E. E. Marbaker. J. Amer. Chem. Soc.,
1915, 37, 86—95.

To the boiling solution of sodium tungstate and
molybdate a definite amount (20 c.c. for 0·15 grm.
WO_3) of stannous chloride solution is added
(50 grms. $SnCl_2,2H_2O$ in 200 c.c. of concentrated

hydrochloric acid). After brief boiling, settling,
and decantation of the clear supernatant liquid
through a filter, the blue precipitate (W_2O_5) is
washed by decantation with hot 5% hydrochloric
acid until the washings fail to give the zinc and thio-
cyanate test for molybdenum. It is then drained
upon the filter, which after a rough drying is gently
ignited in a weighed porcelain crucible and the
tungsten weighed as WO_3. With large amounts
of the metals the concentrated filtrate and washings
are diluted to 250 c.c. and an aliquot part (50 c.c.)
is treated with 20-mesh zinc (5 to 10 grms.) for
about 10 minutes. The filtrate and washings
from the precipitated tin contain the whole of the
molybdenum as green Mo_2O_3. The flask of a
Jones reductor is charged with 20 c.c. of ferric
ammonium sulphate solution (10%) and 20 c.c.
of the " titrating solution " (90 grms. of manganous
sulphate, 650 c.c. of distilled water, 175 c.c. of
syrupy phosphoric acid, and 175 c.c. of concentrated
sulphuric acid). The following solutions are then
passed successively through the reductor into the
flask: 50 c.c. of dilute hydrochloric acid (2·5%
HCl by vol.), the molybdenum solution at 60° C.,
150 c.c. of dilute hydrochloric acid, and 150 c.c.
of hot distilled water. The ferrous iron in the
mixture is finally titrated quickly with $N/10$ per-
manganate solution : the process is not hindered
by the various colour changes which occur.
Tungsten in sodium tungstate is determined by
adding sodium chloride and proceeding as when
molybdenum is present.—J. R.

Indicators, etc.; Notes on recent——. G. S.
Walpole. Biochem. J., 1914, 8, 628—640.

THIS compilation of information on indicators,
regulator mixtures, etc., includes a chart of
hydrogen ion concentration data representing the
sensitive ranges of all the indicators in general use,
both in colorimetric and " end-point " processes.
2.5-Dinitroquinol (Henderson and Forbes, J.
Amer. Chem. Soc., 1910, 32, 687) is green in dilute
acid, yellowish at $P_H^+ = 3$, reddish brown at abso-
lute neutrality, and purple at $P_H^+ = 9·5$, and thus
is effective over the ranges of methyl orange,
litmus, and phenolphthalein. The range of
di-o-hydroxystyryl ketone, or lygosin (Ferenez,
this J., 1914, 1075) brownish yellow to green,
is identical with that of α-naphtholphthalein
($P_H^+ = 7·3$ to 8·7). 1-Oxynaphthochinomethane
(Nierenstein, private communication) is colourless
at $P_H^+ = 2·7$, and shows a gradual increase of
purple colour to $P_H^+ = 3·7$; it gives the sharpest
colour changes of any indicator working in this
region. 6-Sulpho-α-naphthol-1-azo-m-hydroxy-
benzoic acid (Mellet, this J., 1910, 1274; 1911,
1186) changes from orange to blue between $P_H^+ = 7$
and 8, and from violet to red between $P_H^+ = 12$ and
13. 2.6-Dinitroaminophenol, or isopicramic acid
(Meldola and Hale, Chemical World, 1912, 1, 327)
is pink in solutions more acid than $P_H^+ = 4·1$ and
yellow in solutions more alkaline than $P_H^+ = 5·6$.
Alizarinmonosulphonic acid (Knowles, this J.,
1907, 489) is more sensitive than methyl orange
between $P_H^+ = 3·7$ (yellow) and $P_H^+ = 4·2$ (pink).
Extract of red cabbage (Walbum, Biochem. Zeits.,
1913, 48, 29; Comptes rend. Lab. Carlsberg, 1913,
10, 227), which has a sensitive range from $P_H^+ = 2$
to 4·5, may be used in presence of proteins,
neutral salts, toluene etc. The behaviour of the
yellow dye from mimosa flowers (Robin, this J.,
1904, 561) suggests its possible identity with
turmeric. The hydrogen E.M.F.'s of the following

"regulator mixtures" have been determined: cacodylic acid-sodium cacodylate, acetic acid-sodium acetate, hydrochloric acid-sodium acetate. Lists of references to data on isoelectric points, optimum reactions for enzymes, and reactions of physiological fluids are given.—J. R.

Instrument for measuring flame velocities in gas and dust explosions. Morgan. *See* IIA.

Determination of ash in coal and coke. Weisser. *See* IIA.

Determination of hydrogen sulphide in coal-gas. Way. *See* IIA.

Some properties of solutions of the boric acids in alcohol. A modified boiling point apparatus. Firth and Myers. *See* VII.

Rapid detection of cyanides, thiocyanates, ferro- and ferricyanides. Feigl. *See* VII.

Tri-ammonium citrate. Hall. *See* VII.

Determination of peroxide in commercial lead oxide. Dean. *See* VII.

Determination of sulphur in rubber. Gaunt. *See* XIV.

Note on the analysis of cube gambier. Bennett. *See* XV.

Chemical control in the cane sugar factory, using boiling-house balances of both sucrose and total solids. Johnson. *See* XVII.

Presence of free pentoses in plant extracts and the influence of other sugars on their determination. Davis and Sawyer. *See* XVII.

Hydrolysis of maltose by hydrochloric acid under Herzfeld conditions of inversion. Davis. *See* XVII.

Detection of sulphurous acid in the atmosphere by means of mercury salts. Deniges. *See* XIXB.

Determination of silicic acid in natural waters. Winkler. *See* XIXB.

Composition and analysis of lime-sulphur sprays. Ramsay. *See* XIXB.

Delicate reaction for apomorphine. Grimbert and Leclère. *See* XX:

Determination of cineol in eucalyptus oil. Turner and Holmes. *See* XX.

PATENTS.

Detecting, indicating, and recording the presence and proportions of gas in the atmosphere of mines. Eng. Pat. 29,094. *See* IIA.

Apparatus for measuring the amount of suspended impurity in the air. Eng. Pat. 8725. *See* XIXB.

XXIV.—MISCELLANEOUS ABSTRACTS.

Clintonia borealis ; Fruit of ——. H. A. Slippy. Chem. News., 1915, 111, 2—3.

THE berries yielded 4·87% ash, and contained 1·05% nitrogen, 13·2% sugar consisting of glucose

and lævulose, and over 4% of oil, as well as small amounts of citric and tartaric acids. The light yellow oil had a sweetish taste, and could not be easily saponified. Its sp. gr. was 0·897 at 15·5° C. and saponification equivalent 418.—R. G. P.

Trade Report.

Prohibited exports.

A ROYAL Proclamation, dated February 3rd, 1915, consolidates and supersedes all previous Proclamations or Orders of Council under Sect. 8 of the Customs and Inland Revenue Act, 1879, the Exportation of Arms Act, 1900, and the Customs (Exportation Prohibition) Act, 1914 (see this Journal, 1914, 810, 846, 896, 988, 1038, 1118, 1230).

The new Proclamation contains the following :— (A) *The exportation of the following goods is prohibited to all destinations :*—Non-inflammable "celluloid" sheet (or similar transparent material non-soluble in lubricating oil, petrol or water); aeroplane dope ; fusel oil (amyl alcohol) ; amyl acetate ; aceto-celluloses ; triphenyl phosphate; carbons, suitable for searchlights ; cartridges, charges of all kinds, and their component parts; chemicals, drugs, dyes and dyestuffs, medicinal and pharmaceutical preparations, and tanning extracts, namely :—acetone ; acetylsalicylic acid (aspirin) ; ammonium nitrate, perchlorate, and sulphocyanide ; antipyrine (phenazone) ; anti-tetanus serum ; barium chlorate ; belladonna and its preparations and alkaloids ; calcium acetate and all other metallic acetates ; calcium nitrate; cantharides and its preparations ; carbolic acid; chloral and its preparations, including chloramid; coal tar distillation products, namely, benzol and cresol and the fractions of the distillation products of coal tar between benzol and cresol ; coal tar products for use in dye manufacture, including aniline oil and aniline salt ; collodion ; cresol, all preparations of (including cresylic acid) and nitro-cresol (except saponified cresol) ; cyanamide ; diethylbarbituric acid (veronal) and veronal sodium ; dimethylaniline ; dyes and dyestuffs manufactured from coal tar products ; emetin and its salts ; ergot of rye, not including liquid extract or other medicinal preparations of ergot ; eucaine hydrochlor.; gentian and its preparations; henbane and its preparations ; hydroquinone ; indigo, natural ; ipecacuanha root ; methylaniline ; neo-salvarsan ; nitric acid ; nitrotoluol ; novocain ; opium and its preparations and alkaloids ; paraffin, liquid medicinal ; paraformaldehyde and trioxy-methylene ; " Peptone Witte " ; peroxide of manganese ; phenacetin ; picric acid and its components ; potash salts, namely, chlorate, cyanide, nitrate, permanganate ; protargol, not including silver proteinate ; saccharin (including " saxin "); salicylic acid and salicylate of soda ; salol ; sal-varsan ; santonin and its preparations ; sodium chlorate and perchlorate ; sulphonal ; sulphur; sulphuric acid ; tanning extracts, viz., chestnut extract, oakwood extract ; thorium nitrate ; thymol and its preparations ; trional ; valonia ; explo-sives of all kinds ; brewers' and distillers' grains ; brewers' dried yeast ; cakes and meals ; glass for optical instruments.

(B) *The exportation of the following goods is prohibited to all destinations abroad other than British Possessions and Protectorates :*—Chemicals, drugs, medicinal and pharmaceutical prepara-tions, acetanilide, aconite and its preparations and alkaloids ; alcohol, methylic ; alumina and salts of aluminium ; ammonia, liquified ; antimony, sulphides and oxides of ; benzoic acid (synthetic) and benzoates ; bromine and alkaline bromides ; coca and its preparations and alkaloids ; copper,

suboxide of; copper sulphate; cresol (saponified); formic aldehyde; fulminate of mercury; glycerine, crude and refined; hexamethylene tetramin (urotropin) and its preparations; hydrobromic acid; potash, caustic; potassium bicarbonate, bichromate, carbonate, chloride, metabisulphite, prussiate, and sulphate (including kainit); chrome alum; sodium nitrate; tartaric acid and alkaline tartrates; zinc sulphate; ferro alloys, including ferro-chrome, ferro-manganese, ferro-molybdenum, ferro-nickel, ferro-titanium, ferro-tungsten, ferro-vanadium, spiegeleisen; ferro-silicon; graphite including foundry (moulding) plumbago and plumbago for lubricating; the following metals and ores, viz.:—aluminium and alloys of aluminium; antimony and alloys of antimony; bauxite; chrome ore; cobalt; copper and its alloys; lead (including solder containing lead); lead ore; manganese and manganese ore; mercury; molybdenum and molybdenite; nickel and nickel ore; scheelite; selenium; tungsten; vanadium; wolframite; zinc and zinc ore (including zinc ashes, spelter, spelter dross, and zinc sheets); mica (including mica splittings) and micanite; mineral jellies; oil, blast furnace (except creosote and creosote oil); oil fuel, shale; oil, mineral lubricating (including mineral lubricating grease and lubricating oil composed of mineral and other oils); oils, all vegetable (other than linseed oil, boiled and unboiled, unmixed with other oil, and not including essential oils); oil, whale, namely train. blubber, sperm or head matter, and seal oil, shark oil, and Japan fish oil; oleaginous nuts, seeds and products, the following, namely:—castor beans, coconuts, copra, cotton seed, ground nuts (arachides), linseed, palm kernels, rape seed, sesame seed, and soya beans; oleo oil, " Premier jus," and animal tallow; petroleum, fuel oil (including turpentine substitute and paraffin oil); petroleum, gas oil; petroleum spirit and motor spirit (including shell spirit); malt; margarine; sugar, refined and candy; sugar, unrefined; rubber (including raw waste and reclaimed rubber) and goods made wholly of rubber; turpentine (oil and spirit);

(c) *The exportation of the following goods is prohibited to all foreign ports in Europe and on the Mediterranean and Black Seas, other than those of France, Russia (except Baltic ports), Belgium, Spain and Portugal:*—Asbestos; camphor; bismuth and its salts; iodine and its preparations and compounds; mercury, salts and preparations of; nux vomica and its alkaloids and preparations; india-rubber, sheet, vulcanised; copper ore; iron ore; iron, hæmatite pig; iron pyrites; rosin.

Permits to import " enemy goods," Brit. and Col. Drug., Jan. 15 and 22, 1915.

THE Board of Trade has granted licences to import certain goods under Par. 8 of the " Trading with the Enemy Proclamation, No. 2," of Sept. 9, 1914; among the articles in respect of which licences have been given are :—

Chemicals (general):. Antimony fluoride, barium peroxide, beta-naphthol, carbolic acid crystals, chloral hydrate, chromium fluoride, chromium oxalate, formaldehyde, gallic acid, magnesium chloride, oxalic acid, paraldehyde, pyrogallic acid, tannic acid, tartar emetic, thorium nitrate. *Fine chemicals:* Acetanilide, aceto-salicylic acid, salicylic acid, salol, sodium salicylate, atophan, atropine, chlorophyll, eucaine hydrochloride, eucaine lactate, heliotropin, hexamethylene-tetramine, hydroquinone, para-amido-phenol, phenacetin, piperazine, safrol, scarlet red, salvarsan, neo-salvarsan, terpineol, thymol, vanillin. *Glassware, etc.:* Optical glass, chemical apparatus, glass for syphons, glass bulbs for X-ray work. *Lanoline. Potassium compounds:* Kainit and the following salts:—Salts (general), bichromate, bromide, carbonate, caustic, chlorate, cyanide, meta-bisulphite.

muriate, permanganate, prussiate, prussiate (yellow), sulphate. *Vegetable drugs:* Belladonna (root and leaves), colchicum (seeds and corms), dandelion, digitalis, henbane, insect flowers, juniper berry oil, valerian.

Applicants, who should address the Assistant Secretary, Commercial Department, Board of Trade, Whitehall, S.W., will have to prove that the articles they desire to import are practically the exclusive product of Germany, Austria-Hungary, or Turkey, and the goods would be imported through a " neutral " agent. The licence confers the right " to purchase, import, and contract for " the articles in question, and is subject to modification or revocation at any time in accordance with the condition of stocks or possible new production in this country.

Export of articles for the French Government. Board of Trade Announcement, Jan. 29, 1915.

APPLICATION for permission to export to France goods of which the export is prohibited by Proclamation, will receive special consideration if it can be clearly shown that the goods are destined for the use directly or indirectly of the French Government. Such applications must be made to the Commission Internationale de Ravitaillement, India House, Kingsway, W.C. Documents issued by provincial military or naval officers, other local authorities, or Government contractors in France will not be recognised as evidence of the destination of the goods unless formally approved in writing by the competent Department of the French Government.

Applications for permission to export goods which are ordered by firms or individuals in France for purely industrial purposes and which are not destined for the use of the French Government, will continue to be made in the ordinary manner to the Commissioners of Customs and Excise, Custom House, E.C.

Australia's trade with Germany.

A PAMPHLET has been issued from the offices of the Commonwealth of Australia, 72, Victoria Street, London, S.W., giving details of the trade between Australia and Germany. Among the exports from Australia to Germany in 1913 were the following :— Wool, £4,693,167; copper, £367,235; tannin bark, £23,653; lead, £37,094. The figures for " ores and concentrates " and " specie " for 1913 are not given, but for 1912 these amounted to £586,152 and £400,351 respectively. Australia imported the following from Germany in 1913 :— Ale and beer, £133,446; arms and explosives, £1,702,145; drugs and chemicals, £266,811; glass and glassware, £152,817; metal and metal manufactures, £2,030,674.

The pamphlet also contains a list of exporters of Australia's principal products.

New Customs and Excise Tariffs of the Commonwealth of Australia. Board of Trade J., Jan. 21, 1915. Supplt., price 3d.

THE new Tariff rates of the Commonwealth of Australia came into force on December 3 last. The duty on ale and other beer, cider, etc., containing more than 2% proof spirit is increased 6s. per gall., spirits and spirituous liquors not otherwise specified, amyl alcohol not denatured in accordance with departmental by-laws, essences, fruit ethers, tinctures, etc., containing more than 75% proof but not O.P., sulphuric ether containing 5% or more proof spirit, still wine containing more than 40% proof spirit, and other wines containing more than 50% proof spirit are now dutiable at 17s. per gall. (formerly 14s.). Other spirituous liquids are increased in a corresponding proportion. Fancy or medicated toilet soap is

increased from 4d. to 5d. per lb. or from 25 % to 30 %, ad val., whichever is higher, and other unspecified soaps, including compounded detergents and soap substitutes, but not including saponaceous disinfectants, have risen from 25 % to 30 % ad val. The duty on varnishes, oil and varnish stains, lacquers, liquid sizes, gold size, oil and wood finishes, lithographic varnish, printer's ink reducer, terebine, liquid driers, and liquid stains for wood is raised from 2s. to 2s. 6d. per gallon ; paints, ground in liquid, rise from 4s. to 5s. per cwt. in respect of packages containing over 14 lb. and from 6s. to 7s. 6d. or 15 % to 20 % ad val. for smaller packages. Filters are changed from 15 % to 20 % ad val. Boric acid has been altered from 20 % ad val. to 7s. per cwt. ; opium extracts, which formerly were not specified, are now 60s. per lb. ; artificial perfumes (synthetic) concentrated, containing less than 2 % proof spirit, are now 3s. per fluid ounce, or free of duty when used for manufacturing purposes under departmental by-laws.

* New Books.

[The Roman numerals in thick type refer to the similar classification of abstracts under "Journal and Patent Literature" and in the "List of Patent Applications."]

I. *Gas and oil engines*, Care and repair of. N.Y., Industrial Press. c. 48 p. 8vo. pap. 1915. 25c.

Goodenough, G. A.: Thermal properties of steam. Illinois Univ. Bull. No. 75. 8vo. swd. Chapman and Hall. London. 1915. Net 1s. 9d.

Gould, G. B., and *Hubbard*, C. W.: The cost of power. N.Y., Fuel Engineering Co. of N.Y. c. 125p. il. pls. diagrs. 16mo. 1914. $2.

IIA. *Fieldner*, A. C.: Notes on the sampling and analysis of coal. Wash. D.C., Gov. Pr. Off. 61 p. il. 8vo. (U.S. Bu. of Mines, Techn. pap. 76.) 1914.

Parr, S. W. and *Hadley*, H. F.: The analysis of coal with phenol as a solvent. Urbana. Ill. Univ. of Ill. 41 p. il. pls. tabs. (Eng. Exp. Stat. bull.) pap. 1914. 25c.

Williams, R. Y.: The humidity of mine air ; with especial reference to coal mines in Illinois. Wash. D.C., Gov. Pr. Off. 69 p. tabs. pls. map. diagrs. 8vo. (U.S. Bu. of Mines, bull. 83.) 1914.

White, D. and *Thiessen*, R.: The origin of coal ; with a chapter on the formation of peat, by C. A. Davis. Wash. D.C., Gov. Pr. Off. 10 +390 p. pls. 8vo. (U.S. Bu. of Mines, bull. 38.) 1914.

Gas works directory and statistics. 1914—1915. Cr. 8vo. pp. 548. Hazell, Watson and Viney. London. 1915. Net 10s. 6d.

Oil and gas fields in 1913. U.S. Geological Survey. Base map of the United States, in scale of 1: 2,500,000. In 2 sheets 40+50. Wash. D.C. Off. of Survey. pap. 1915. $1.

IV. *Wahl*, A.: The manufacture of organic dyestuffs. auth. tr. by F. W. Atack. N.Y., Macmillan. 14+338 p. (bibls.) 12mo. 1915. $1.60 n.

VII. *Calvert*, A. F.: Salt in Cheshire. 8vo. Spon. London. 1915. Net 21s.

Levy, S. I.: The rare earths, their occurrence, chemistry and technology. 8vo. pp. 360. E. Arnold. London. 1915. Net 10s. 6d.

Soddy, F.: The chemistry of the radio-elements. 2 parts in one vol. 8vo. pp. 212. limp. Net 5s. 6d.

Ditto. Part 1. new ed., revised and enlarged. Longmans. London. 1915. Net 4s.

IX. *Landini*, A.: Le costruzioni in cemento armato. Bologna. 8vo. fig. p. 288. Lire 10.

Searle, A. B.: Bricks and artificial stones of non-plastic materials : their manufacture and uses. 4to. Churchill. London. 1915. Net 8s. 6d.

X. *Park*, J. Prof.: A text-book of practical assaying. Revised and enlarged from third New Zealand edition. Authorised text-book for New Zealand Government Schools of Mines. With illustrations. Crown 8vo. Ch. Griffin. London. 1915. Cloth. 7s. 6d. net.

Wraight, E. A.: Assaying in theory and practice. N.Y., Longmans. 11+323 p. il. tabs. figs. O. 1915. $3 n.

Wysor, H.: Metallurgy : a condensed treatise for those desiring a general knowledge of the subject. 2nd ed. Easton, Pa., Chemical Pub. c. 13+391 p. il. diagrs. 8vo. 1915. $3.

XII. *Copeland*, E. B.: The cocoa-nut. N.Y., Macmillan. 13+212 p. il. 8vo. 1915. $2.60 n.

XVIII. *Brannt*, W. T. ed.: A practical treatise on the manufacture of vinegar. 3 ed. rev. Phil. H. C. Baird and Co. 567 p. il. 8vo. 1915. $6 n.

XIXB. *Barker*, A. H.: The theory and practice of heating and ventilation. N.Y., Van Nostrand. 656 p. il. tabs. 8vo. 1915. $8 n.

Harrington, C.: A manual of practical hygiene for students, physicians, and health officers. Fifth edition. Revised and enlarged by M. W. Richardson in collaboration with officials connected with the Massachusetts State Board of Health. With 24 plates in colours and monochrome and 125 engravings. 8vo. Lea and Febiger. New York. 1914. Cloth. $5.00 net.

Woodman, A. G., and *Norton*, J. F.: Air, water, and food from a sanitary standpoint. 4th ed., rev. and rewritten. N.Y., Wiley. c. 5+248 p. il. 8vo. 1915. $2 n.

XXI. *Pizzighelli*, G.: I processi fotografici positivi. Milano. 16mo. fig. p. XVI. 398. 1914. Lire 4.

Photography, American Annual of, 1915. Vol. XXIX. Edited by P. Y. Home. 8vo. swd. Routledge. London. 1915. Net 3s. 6d.

XXIII. *King*, L. V.: On the conversion of heat from small cylinders in a stream of fluid. Determination of the conversion constants of small platinum wires with applications to hot-wire anemometry. (Roy. Soc.). 4to. pp. 60. Dulau. London. 1915. Net 4s.

XXIV. *Arndt*, K.: A popular treatise on the colloids in the industrial arts: tr. from the 2nd enl. German ed. by N. E. Katz. Easton, Pa., Chemical Pub. c. 6+73 p. 12mo. 1914. 75c.

Noyes, A. A., and *Sherrill*, M. S.: A course of instruction in the general principles of chemistry. Bost., Todd. c. 130 p. diagrs. 8vo. 1914. $2.

Ransom, J. H.: General chemistry. Lafayette. Ind. (Murphey-Bivins Co.) c. 312 p. diagrs. 8vo. 1914. $1.75.

Handbook of chemistry and physics ; a ready-reference pocket book of chemical and physical data ; from the most recent authoritative sources. Chemical Rubber Co., Cleveland, O. c. 322 p. il. tabs. 12mo. 1914. $2.

Year-Book of the Scientific and Learned Societies of Great Britain and Ireland. 1914. 8vo. pp. 384. C. Griffin. London. 1915. Net 7s. 6d.